EVALUATION OF ANAEROBIC MEMBRANE BIOREACTORS AND HYDROTHERMAL CATALYTIC GASIFICATION FOR ENHANCED CONVERSION OF ORGANIC WASTES TO RENEWABLE FUELS

BY

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THESIS

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ABSTRACT

Anaerobic membrane bioreactor (AnMBR) systems, merging anaerobic digestion with membrane filtration technology, have been studied as an alternative wastewater treatment process that can effectively generate energy while removing particulates and organics in a single process. AnMBR studies with municipal wastewater have observed high COD removal rates typically in the range of 72 – 94%, and methane yields higher than can be achieved with conventional anaerobic digesters. In this paper, routine bioaugmentation—the repeated addition of externally cultured microorganisms into the process stream—was tested as a means to increase hydrolysis and acid-production with the aim of thereby improving methane yields. The effects of bioaugmentation were tested in a pilot-scale continuous two-phase AnMBR system with a submerged (vacuum-driven) membrane in the methane-phase reactor. The acid-phase reactor was operated with a hydraulic retention time (HRT) and solids retention time (SRT) of 2.5 days, whereas the methane-phase reactor used an HRT between 15.2 – 18.3 days and an SRT between 79 – 92 days. With an organic loading rate (OLR) of 2.5 g-COD/L/day and bioculture addition to the acid-phase reactor at a dose of 3.9% of influent volatile solids, the acid-phase SCOD concentrations were increased by 56%, and total VFA concentrations were increased by 111%, indicating improved solubilization and acid-production. However, total methane yield was about 12% lower with bioaugmentation—423 ± 8 ml/g-VS without bioaugmentation and 372 ± 28 ml/g-VS with bioaugmentation. However, this difference was only statistically significant at a ≤ 78% confidence interval. The higher variability and minor decrease in methane production with bioaugmentation was correlated with higher production of hydrogen sulfide in the methane-phase, which could be explained by propionate and acetate accumulation in the acid-phase. The biological reactions of sulfate-reduction are more energetically favorable than those of acetogenesis and aceticlastic methanogenesis. Thus, sulfate-reducers can grow faster using these substrates than competing methanogens. After stopping bioaugmentation, the AnMBR system performance improved to achieve 98% of the theoretical maximum methane yield. It was found that bioaugmentation can have a neutral or slightly negative effect on an AnMBR system that is already achieving a high level of organics destruction without bioaugmentation. Both with and without bioaugmentation, the AnMBR system maintained > 99% COD removal while feeding a highly concentrated feedstock of 42 – 44 g-COD/L at a range of OLRs between 0.73 – 4 g-COD/L/day, resulting in an effluent COD concentration of

300 – 400 mg/L. High COD removal and methane yields (99.4% and 89.2%, respectively) were also achieved at a higher OLR of 5.1 g-COD/L/day, although membrane fouling inhibited consistent operation at this high OLR during this study.

This document also investigates the application of subcritical hydrothermal catalytic gasification (HCG) as an alternative to anaerobic digestion. HCG of a lignocellulosic feedstock (newspaper) with Raney nickel (Ra-Ni) catalyst at 350°C for 30 minutes was capable of gasifying the feedstock into a combustible syngas, but the catalyst lifetime was far too low for economic feasibility. However, tests with routine addition of NaOH as a secondary catalyst showed high, consistent methane and energy yields by means of in-situ reactivation of Ra-Ni, which was designed upon the same principles of ex-situ Ra-Ni regeneration. At these yields, HCG was shown to potentially be economically viable. In-situ synthesis of Ra-Ni was also tested in order to lower operating costs, and increase safety by eliminating the need to store a pyrophoric material. Experiments showed that the activity of in-situ synthesized Ra-Ni catalyst was equivalent to or higher than that synthesized ex-situ. This could possibly be explained by the beneficial presence of bayerite during in-situ synthesis. Based upon the consistent energy yields achieved with routine NaOH addition, a comparison of HCG to literature reports of conventional AD was made. This analysis found that HCG could extract 40% of the newspaper's energetic content while conventional AD could only achieve up to 18% (21% of theoretical methane). However, HCG's higher heating requirements may lead to AD being more energetically favorable when processing organics with high moisture contents. Further analysis with newspaper feedstock, taking into account operational heating and catalyst embedded energy costs, showed that HCG is more favorable than conventional AD. At newspaper's original moisture content of 8%, net energy production is roughly 2 times greater with HCG than AD. HCG is also advantageous because of its ability to process material on the timescale of 30 – 60 minutes while AD typically takes 20 – 40 days. Thus, HCG reactors are significantly smaller and can convert material that might otherwise remain unused for AD. However, the heat input for HCG is much higher than anaerobic digesters. As a result, when processing wet feedstocks, HCG would need to have a heat recovery system to be competitive with the net energy produced by anaerobic digestion. Overall, HCG with Ra-Ni and routine NaOH addition is a promising thermochemical alternative to biological anaerobic digestion processes, and has shown potential for economic viability and energy-positive operations. Further work should be conducted to

minimize the amount of NaOH needed and maximize Ra-Ni lifetime, which are currently HCG's greatest energy burdens.

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I will cherish the newfound knowledge and experiences that I have been privileged to gain over these past two years at UIUC, and be sure to use them to the best of my abilities in future endeavors. And so, as I begin another transition, I shall ask myself "What?…So what?…Now what?"

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ABBREVIATIONS

AnMBR	Anaerobic membrane bioreactor
AP	Acid phase
CHN	Carbon, hydrogen, nitrogen
COD	Chemical oxygen demand
EJ	Exajoules (10^{18} joules)
Feed:Catalyst ratio	Feed-to-catalyst ratio, on a dry weight basis
HCG	Hydrothermal catalytic gasification (subcritical, < 374°C, water medium)
HRT	Hydraulic retention time
HSWW	High-strength wastewater
LSWW	Low-strength wastewater
MP	Methane phase
MSW	Municipal solid waste
OLR	Organic loading rate
PS	Primary sludge
SCOD	Soluble chemical oxygen demand
SRT	Solids retention time
TCOD	Total chemical oxygen demand
TS	Total solids
VFA	Volatile fatty acids
VS	Volatile solids

CHAPTER 1

INTRODUCTION

Human heartbeat – 0.5-2 J

Fully charged iPhone $5 - 34 \times 10^3$ J

Driving a Honda Civic 16 miles to work – 6×10^7 J

Putting a space shuttle into orbit – 10^{13} J

World energy consumption in 2010 – 3.6×10^{20} J

By 2050, the UN estimates a 35% global population increase to 9.3 billion people (UNPD, 2010). In order to provide basic services to these additional people, global energy demand is expected to rise by at least 36 EJ (3.6×10^{19} J) given anticipated improvements in energy efficiency and conservation, and could rise by as much as 227 EJ without those improvements (Teske et al., 2011). To put this into perspective, global energy consumption in 2010 was 363 EJ (IEA, 2012). The problem of increasing energy demands is further compounded by its consequences. The current energy production paradigm relies primarily on the burning of fossil fuels, consuming within seconds a product that took the Earth's geological processes eons to create. This approach guarantees that the supply of fossil fuels will eventually be depleted, whether it be within the next hundred or thousand years—and many studies estimate some fossil fuels will be exhausted within this century. In order to ensure the continuation and advancement of the world's energy-dependent lifestyle, renewable and sustainable energy generation systems must be developed.

One especially harrowing outcome of increasing energy demands is the multitude of negative environmental effects stemming from vast greenhouse gas emissions. The current distribution of energy sources dominated by coal and petroleum points to the fact that increasing energy demands will introduce considerable amounts of CO_2 into the atmosphere, with estimates that anthropogenic CO_2 emissions worldwide will increase more than 60% by 2050 (Teske et al., 2011). A large body of evidence supports the theory that heightened atmospheric CO_2 concentrations will lead to global climate change and more extreme weather patterns (Hurrell, 1995; Kalnay et al., 1996; Zachos et al., 2001). The implications of climate change can disrupt

terrestrial and aquatic ecosystems worldwide and threaten the normal functioning of both local communities and global markets (Howden et al., 2007; Parmesan and Yohe, 2003). To minimize atmospheric pollution and mitigate diminishing energy resources, clean sustainable energy generation technologies must be developed and implemented.

Population growth will also increase demands on wastewater treatment and landfilling. As it stands, water and wastewater treatment are highly energy-intensive processes which draw about 3 – 4% of total US electricity consumption, equivalent to 56 billion kWh or 2×10^{17} J (US EPA, 2012). Rising water demands and concerns of water shortage warrant the development of more efficient and versatile treatment methods. Since municipal wastewater solids are primarily composed of organic matter, they can potentially be repurposed for renewable bioenergy production. One such technology that addresses both ends of the water-energy nexus is anaerobic digestion. Anaerobic digestion is a biological process by which anoxic microorganisms metabolically break down organic molecules and convert them into methane gas. Anaerobic digestion processes can be more economical than conventional wastewater treatment methods owing to the generation of burnable gas (Ghangrekar and Kahalekar, 2003). As of 2008, only 1,351 of the 3,171 U.S. wastewater treatment facilities with flows above 1 million gallons per day were operating anaerobic digesters, with merely 203 utilizing their digester gas for heating or power. If all 1,351 treatment plants were to utilize their digester gas, approximately 1.3×10^{16} J could be generated (Eastern Research Group, Inc. and Resource Dynamics Corporation, 2011). An improvement to anaerobic digestion systems is the advent of membrane bioreactors, applying membrane filtration techniques to anaerobic digesters. Anaerobic membrane bioreactors can provide energy savings by reducing the need for biological aerobic removal of wastewater biosolids, disinfection of wastewater, and can potentially turn wastewater treatment plants into net energy producers (McCarty et al., 2011).

As for municipal solid waste (MSW), US MSW generation fortunately appears to have peaked and is starting to show a downward trend as more products are being recycled and reused. Nevertheless, MSW will continue to accumulate in landfills. The majority of this waste is organic, and can be redirected to energy conversion systems, which is readily apparent from landfill methane emissions (Fourie and Morris, 2004; Trégourès et al., 1999). Value can be gained by effectively utilizing MSW as an energy resource, thereby reducing the volume of landfilled waste while also providing renewable energy.

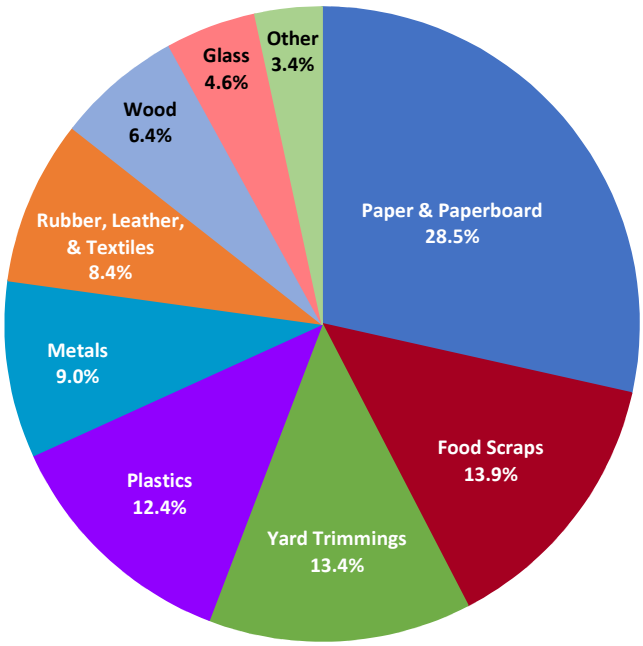

Figure 1.1 2010 Total US Municipal Solid Waste Generation, adapted from US EPA (2011)

An attractive bioenergy feedstock within MSW is paper. Paper has comprised the largest fraction of U.S. municipal solid waste for more than 15 years (Figure 1.1), and is the major component—around 40%—of landfills by weight (Suflita et al., 1992). A significant fraction of paper waste is newspaper. However, newspaper can be particularly difficult to biologically degrade as evidenced by fragments being found that are as old as the landfills they are in. Yuan et al. (2012) observed that paper with higher lignin-content had lower digestion yields, and that newspaper had the highest lignin content (23.4%) compared to cardboard (17.8%) and office paper (1.4%). Therefore, newspaper was found to be the least anaerobically digestible type of paper. Other studies affirm that anaerobic digestion processes poorly degrade newspaper, and achieve low methane yields typically only 21 – 23% of the theoretical potential (Clarkson and Xiao, 2000; Tong et al., 1990; Xiao and Clarkson, 1997). It should be noted that the low digestibility of newspaper is not due to the presence of ink, which in modern times is typically derived from soybean oil and may actually contribute to the methane yield (Stinson and Ham, 1995). Various types of pre-treatment can increase newspaper digestibility, but they remain far from the maximum potential (Table 1.1). In these situations where biological degradation is inefficient and pretreatment methods are only mildly effective, alternative conversion technologies should be explored.

Table 1.1 Anaerobic Digestion of Pretreated Newspaper

Pretreatment	HRT (days)	Conversion	Reference
Microbial: MC1	12	33% methane yield	(Yuan et al., 2012)
Chemical: 35% acetic, 2% nitric acid	60	57% methane yield	(Xiao and Clarkson, 1997)
Temperature: 190 °C	60	59% TCOD conversion	(Fox and Noike, 2004)

A prospective alternative to anaerobic digestion is hydrothermal catalytic gasification (HCG). HCG is a thermochemical process by which organic matter reacts with a catalyst under high heat and pressure (typically >300 °C and >1246 psi) which maintain all moisture in the liquid phase. The end product consists primarily of a gas mixture (carbon dioxide, methane, and hydrogen), along with residual char and ash. In the absence of an HCG catalyst, the primary product would be an aqueous mixture that resembles crude oil (Yu, 2012). HCG processes can achieve high gasification efficiencies of more than 90% at relatively low reaction times—within minutes to hours—with assorted biomass feedstocks including lignocellulosic materials (Azadi et al., 2012; Elliott, 2008). However, as an emerging technology that is more nascent than anaerobic digestion, HCG requires significantly more research and pilot-studies before mainstream application. The majority of current research on HCG focuses on determining the conversion yields for different feedstock and catalyst combinations under various operating conditions. Further work is necessary to explore catalyst lifetime and continuous operation to assess HCG's true economic viability.

CHAPTER 2

LITERATURE REVIEW FOR ANAEROBIC DIGESTION

2.1 Metabolic Pathways of Anaerobic Digestion

The metabolic process of anaerobic digestion can be divided into four sequential steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Figure 2.1 depicts the various routes and fate of organic material in the anaerobic production of methane. Additional pathways—not shown—are involved in nutrient removal (i.e. the formation of inorganic nitrogenous and sulfurous species such as ammonia and hydrogen sulfide) which compete for the the intermediates of methane production (i.e. volatile fatty acids).

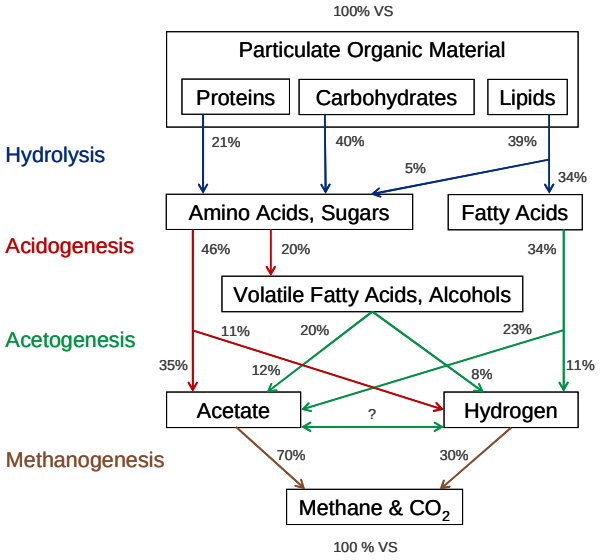

Figure 2.1 Anaerobic digestion pathways, adapted from Gujer and Zehnder (1983)

The first step of anaerobic digestion is hydrolysis: the breakdown of large organic particulates and macromolecules into soluble macromolecular compounds. Hydrolysis is generally characterized by slow reaction rates and is therefore commonly the rate-limiting step of anaerobic digestion (Batstone et al., 2009; Eastman and Ferguson, 1981; Tomei et al., 2009). Hydrolysis rates are dependent upon biomass concentration, extracellular enzyme production, substrate concentration, and the substrate's specific surface area (Brummeler et al., 1991).

Accordingly, difficulties with hydrolysis can be partly attributed to a feed material's large particle size. Following the anaerobic digestion process from start to finish, organic compounds are digested into smaller and smaller pieces. This means that hydrolysis acts on the largest, most complex compounds. These large particulates have a smaller surface-area-to-volume ratio than dissolved soluble compounds, so they have fewer points of access for hydrolytic bacteria, and thus can require more time to degrade (Palmowski and Müller, 2000). Hydrolysis can also be hindered by these compound's chemical and physical structure, such as the crystallinity of solid cellulose (Hall et al., 2010; Jeihanipour et al., 2011). Lignocellulosic materials—composed of cellulose, hemi-cellulose, and lignin—are especially difficult to hydrolyze (Adney et al., 1991; Noike et al., 1985). Hemi-cellulose connects cellulose to lignin which provides rigidity to the lignocellulosic matrix. Hemi-cellulose's covalent bonds with lignin also give plant cell walls their mechanical resistance and protection against pathogens. (Atalla et al., 1993; Salmen and Olsson, 1998). The least hydrolysable material in lignocellulosic materials is lignin—a cross-linked network of hydrophobic polymers that remain insoluble in all solvents (Monties and Fukushima, 2005). Thus, lignin content is widely considered to be the most important indicator of a lignocellulosic material's biodegradability (Chang and Holtzapple, 2000; Monlau et al., 2013).

The second step of anaerobic digestion is acidogenesis: the further breakdown of soluble organics into volatile fatty acids (VFAs)—butyric acid, propionic acid, and acetic acid—by various bacterial species of *Clostridium*, *Enterobacter*, *Syntrophobacter*, and others. VFA concentrations are important indicators of anaerobic digestion performance and should be monitored to ensure there is not significant over-accumulation. VFA overproduction can also be inhibitory or even toxic to methanogenesis, and can induce microbial stress from resulting drops in pH (Neves et al., 2006; Wang et al., 1999). Asides from anaerobic digestion, VFAs also serve as energy and carbon sources for biological nutrient removal (Banerjee et al., 1999). Reduced methane yields are likely to follow from the diversion of VFAs into these alternate pathways, and the products of these pathways can also inhibit anaerobic digestion. It is therefore important that VFAs be efficiently broken down further by the next step of anaerobic digestion.

Through acetogenesis, VFAs are converted into acetic acid and other single-carbon compounds. There are two main pathways by which acetogens produce acetic acid. Syntrophic acetogens degrade VFAs into acetic acid through thermodynamically unfavorable reactions,

while homoacetogens reduce carbon dioxide with hydrogen into acetic acid via the acetyl-CoA pathway (Stams and Plugge, 2009; Wang et al., 2013, 2011).

In the methanogenesis step, aceticlastic methanogens convert acetic acid into methane and carbon dioxide by acetate decarboxylation, while other methanogens convert hydrogen and carbon dioxide into methane. Several of the most common methanogenic genera found in mesophilic conditions include the rods—*Methanobacterium* and *Methanobasillus*—and spheres—*Methanococcus*, *Methanothrix*, and *Methanocarnia* (Visvanathan and Abeynayaka, 2012). Among these, only *Methanothrix* and *Methanocarnia* are aceticlastic. The slow growth rate of methanogens versus other microorganisms has led methanogenesis to be another common rate-limiting step (Ma et al., 2013).

The microbial communities that perform each of these four steps of AD can be highly transient, and can vary considerably with minor shifts in operating conditions. Pervin et al. (2013) observed rapidly changing acid-phase hydrolytic-acidogenic bacterial communities when digesting primary sludge under mesophilic conditions, with only a few species remaining prevalent after increasing the temperature to thermophilic conditions. Methanogens in particular are especially sensitive to changes in environmental conditions, including temperature, pH, nutrient and trace element concentrations, and loading rates. This natural variation can result in unstable and unpredictable reactor performance. One method for producing a more stable hydrolytic-acidogenic microbial population is bioaugmentation.

2.2 Bioaugmentation

Bioaugmentation is the physical addition of externally-cultured microorganisms into a new environment with the goal of increasing the rate of a desired biological process. In the context of anaerobic digestion, bioaugmentation is commonly performed on the acid phase, intending to increase the rates of hydrolysis, acidogenesis, and/or acetogenesis—one of which is generally the rate-limiting step. An infinite number of customized biocultures containing unique mixtures of microorganisms can be created to tailor to specific feedstocks, environments, and conditions.

The conceptual precursor to bioaugmentation can be considered to be enzyme addition. Batch studies have shown with a variety of commercially available enzymes that mesophilic anaerobic digesters with enzyme addition can achieve up to 13.6% greater VS reductions

(Rashed et al., 2010). However, the enzyme loadings used and the results yielded from these studies may not be representative of continuous systems which introduce washout. Higgins and Swartzbaugh (1986) found that the addition of the enzyme cellulase into a continuous, two-phase anaerobic digestion process treating municipal wastewater increased total solids reduction and methane production by 15% and 22%, respectively. However, lipase addition yielded only 2% and 4% increases in total solids reduction and methane production, respectively, although higher enzyme loadings could yield greater advantages. Cinq-Mars and Howell (1977) observed that the addition of *Trichoderma viride* cellulase improved the hydrolysis of municipal wastewater primary sludge in batch experiments, but found no improvement in hydrolysis with fed-batch experiments, likely due to significant inhibition from high product concentrations (Stuck and Howell, 1974). Nevertheless, it has been proven that enzyme addition has the potential to increase hydrolysis and methane production. Therefore, it is logical to suggest that the addition of specialized microorganisms, which themselves produce enzymes, can also improve acid-phase reactions in a similar manner.

In bioaugmentation, the microorganisms that produce the enzymes are themselves added to the process stream. In this way, enzymes can be continuously produced in situ from the growing microbial population. The advantages of bioaugmentation over enzyme addition are that it is less affected by washout due to growth of the bioculture in the applied reactor, and allows the formation of a greater number of active compounds than was originally added. Conversely, biocultures can be more distressed by environmental conditions, and must interact synergistically with the native microbial population in order to thrive and yield any benefits. This was shown by Koe and Ang (1992) who found no significant change in bacterial flora or organics destruction with or without bioaugmentation. In this case, the native microbial population had outcompeted the bioculture. Consequently, when bioaugmenting, it is imperative to both select for competitive bacteria and apply effective dosages. Under optimal conditions and with a proper bioaugmentation culture, greater benefits than with basic enzyme addition are possible.

Numerous studies have reported benefits to anaerobic digestion from bioaugmentation, including increased rates of hydrolysis and acid production. Bioaugmentation has been shown to increase hydrolysis in the acid-phase digestion of cellulosic feedstocks (Martin-Ryals, 2012). Thus, bioaugmentation is likely to increase hydrolysis of municipal wastewater solids, which can

contain up to 20% cellulose from the discharge of toilet paper (Honda et al., 2002, 2000). Increasing the rate-limiting hydrolysis step can thus bring about higher solids reduction and methane yield (Li and Noike, 1992). Bioaugmentation has also been shown to provide odor control by restricting the production of gaseous sulfur compounds (Tepe et al., 2008). Table 3.1 summarizes the benefits observed in several studies on applying bioaugmentation to anaerobic digestion processes.

Table 2.1 Summary of Benefits from Bioaugmenting Anaerobic Digestion Systems

Feedstock	Bioaugmentation Culture	Design	OLR	Temp (°C)	HRT	Benefits	References
Restaurant waste	1.3% VS *Clostridium lundense*	Batch	—	37	10 - 26	28% faster methane yield, 30% decrease in start-up time	(Cirne et al., 2006)
Chicken feathers	2% TS *Fervidobacterium pennivorans*	Batch	—	65	15 - 70	Increase solubilization from 45% to 64%	(Costa et al., 2012)
Nonfat Dry Milk	1.7 mL/day enrichment culture	Semi-continuous	2.7 g-COD /L/day	37	9	70% more methane yield, 35% greater SCOD reduction	(Tale et al., 2011)
Municipal wastewater	5 g/L selected strains of *Bacillus*, *Pseudomonas*, and *Actinomycetes*	Continuous	—	37	18	29% more methane yield, 54% more propionic acid, 37% less CH_3SCH_3	(Duran et al., 2006)
Pig slurry and Sweet sorghum	5% v/v *Enterobacter cloacae*	Continuous	—	37	—	25 – 50% more methane yield	(Kovács et al., 2013)
Pig slurry and Sweet sorghum	5% v/v *Caldicellulosiruptor saccharolyticus*	Continuous	—	55	—	40% more methane yield	(Kovács et al., 2013)
Dairy manure	*Yucca schidigera*	Continuous, Attached-film	0.01 g-VS /L/day	10	—	Improved methane yield	(Vartak et al., 1999)
Distillery waste	10% v/v *M. acididurans*	Continuous, Two-stage	—	26 - 35	5 / 30	12.2% more acid-phase methane, 7.5% more methane-phase methane	(Savant and Ranade, 2004)
Cattle manure	*Caldicellulosiruptor lactoaceticus* and *Dictyoglomus*	Continuous, Two-stage	9 g-VS /day	68 / 55	3 / 12	9% more methane yield	(Nielsen et al., 2007)

2.3 Anaerobic Membrane Bioreactors

Sludge retention mechanisms are known for increasing anaerobic digester performance by retaining biomass (van Haandel et al., 2006). At the highest extreme of sludge retention mechanisms is the anaerobic membrane bioreactor (AnMBR), which combines membrane filtration technology with anaerobic digestion systems. In an AnMBR, effluent is extracted through a membrane that is either internal or external to the methanogenic reactor. The membrane retains solids—greater than 10 nm to 100 μm in diameter—in the system, allowing more time for particulate organics degradation and preventing microbial washout. Hence, the effluent contains only soluble compounds, the majority of which should have already been consumed by methanogens. Consequently, AnMBRs can often achieve >94% TCOD reduction resulting in high effluent quality (Cicek, 2003). AnMBRs have also been shown to have shorter and unproblematic startup periods compared to conventional anaerobic digesters because of their ability to retain microorganisms in the reactor (Fuchs et al., 2003).

By processing effluent through a membrane, the solids retention time (SRT) can now be controlled independently from the hydraulic retention time (HRT). This advantage permits operation at lower HRTs—or, higher flowrates—while still achieving high organics removal and above-average methane yields (Mouthon-Bello and Zhou, 2006). As expected, shorter HRTs and longer SRTs lead to higher biomass concentrations and biogas production (Huang et al., 2011). Longer SRTs have also been shown to increase the hydrolysis of lipids and carbohydrates in conventional digesters (Miron et al., 2000; Young et al., 2013). However, significant membrane fouling will occur at when the HRT is too short, especially when the influent is highly concentrated, and possibly when the SRT is too long when processing poorly degradable solids. Nevertheless, effective anaerobic digestion has been achieved at high reactor solids concentrations of 25 – 30% (Kayhanian and Rich, 1996).

The production of valuable methane gas notwithstanding, AnMBRs are advantageous over conventional MBR treatment since anaerobic sludge is generally easier to filter than raw primary sludge, which leads to higher fluxes and lower system costs. Lawler et al. (1986) found that with effective anaerobic digestion, particles of all sizes are destroyed with preferential removal of small particles which resulted in a loss of specific surface area—the main determinant of sludge dewaterability—and an increase in filterability.

The operation of an AnMBR in two stages, separating acid-phase (AP) reactions from methane-phase (MP) reactions can reap further benefits. Two-stage AnMBR systems can have increased biogas production from enhanced acidogenesis and acetogenesis in the acid-phase reactor (Saddoud and Sayadi, 2007). The membrane treatment is commonly applied to the MP since it is the last step of the anaerobic digestion process. Membrane application to the AP rather than the MP may lead to lower COD removal and decreased efficiency. Kiriyama et al. (1992) only achieved 30-35% COD to gas conversion when membrane treatment was applied to the AP, although volatile suspended solids removal in the AP reactor was a high 84.5% with a 144-day SRT. Nevertheless, AnMBR systems with membrane treatment applied to the MP typically achieve methane yields above 70% and COD removal rates upwards of 90%. Thus, the membrane should process liquid from the MP to garner the best performance.

Table 2.2 presents a literature review of various AnMBR systems, summarizing the COD removal efficiencies and gas yields that were achieved based upon different operating parameters.

Table 2.2 Summary of AnMBR System Performance

Feedstock	OLR (g-COD /L/d)	Design	Membrane Properties	Temp (°C)	HRT (days)	SRT (days)	COD Removal (%)	Methane Yield (ml /g-COD)	Reference
Municipal Wastewater	0.1	Continuous Single-phase	External Hollow-fiber Microfiltration, 0.1 m^2, 0.1 μm pore	—	1	114	72	—	(Baek et al., 2010)
Municipal Wastewater	0.65	Continuous Single-phase	External Framed PES Ultrafiltration, 2 m^2, 38 nm pore	20	0.923	∞	94	240	(Martinez-Sosa et al., 2012)
Primary Sludge	0.98	Continuous Single-phase	External Tubular PES Ultrafiltration, 0.3 m^2, 60 kDa pore	35	20	—	> 60	94	(Ghyoot and Verstraete, 1997)
Domestic Wastewater	1.08 – 4.32	Continuous Single-phase	External Hollow-fiber Microfiltration, 4 m^2, 0.2 μm pore	25	6	30,000	88	—	(Lew et al., 2009)
Synthetic Municipal Wastewater	—	Continuous Single-phase UASB	External Tubular PVDF Ultrafiltration, 0.0625 m^2, 100 kDa pore	—	0.5	∞	80	—	(Salazar-Peláez et al., 2011)
Synthetic Municipal Wastewater	1.1	Continuous Single-phase	External Framed PES Microfiltration, 2 m^2, 0.45 μm pore	25	12	60	98.7	171	(Huang et al., 2011)
Synthetic Municipal Wastewater	1.1	Continuous Single-phase	External Framed PES Microfiltration, 2 m^2, 0.45 μm pore	25	12	∞	97.6	205	(Huang et al., 2011)
Activated Sludge	1.34	Continuous Single-phase	External Tubular Ultrafiltration, 0.2 m^2, 120 kDa pore	—	15	30	—	320[b]	(Dagnew et al., 2010)
Municipal Solid Waste	3.75[a]	Continuous Two-phase	Internal Nylon, 30 μm pore	—	1.5	20	—	210[b]	(Walker et al., 2009)
Cheese Whey	11.39	Continuous Two-phase	External Tubular Ceramic (α-alumin) Microfiltration, 0.4 m^2, 0.2 μm pore	37	4	54.15	98.5	300	(Saddoud et al., 2007)
Methanol	3.1	Continuous Single-phase	Internal Flat-Sheet PVDF Ultrafiltration, 0.03 m^2, 70 kDa pore	37	3.23	230	97	350	(Lin et al., 2009)
Kraft Evaporator Condensate + Methanol	12	Continuous Single-phase	Internal Flat-Sheet PVDF Ultrafiltration, 0.03 m^2, 0.3 μm pore	37	21	—	93	350	(Xie et al., 2010)

[a] (g-VS/L/d) [b](ml/g-VS)

2.3.1. Membrane Properties Relating to Flux and Fouling

Membrane fouling is one of the most significant limitations of AnMBR systems. The majority of current AnMBR research focuses on how to improve and sustain high membrane fluxes. One segment focuses on optimal operating parameters while another investigates the effects of different membrane properties and designs. These membrane properties include pore size, material, electrical charge, water interactions, and physical configuration.

Membranes constructed from organic materials are highly susceptible to biofouling and caking due to being rough and fibrous. However, a cake layer can act as a secondary membrane layer and provide greater rejection of VFAs (Choo and Lee, 1996). Inorganic membranes, in contrast, primarily suffer from struvite caking (Kang et al., 2002). Membrane materials can also carry positive, negative, or neutral charges. In theory, negatively charged membrane should suffer the least from biofouling while positive membranes experience the most biofouling. This is because negatively charged membranes would repel bacteria, which have negatively charged cell walls. In one study, negatively charged membranes could achieve twice the filtration flux of positively charged membranes, resulting from less plugging by suspended particles (Shimizu et al., 1989). In another study, bacteria was found to adhere more readily to positively charged surfaces (Harkes et al., 1991). Consequently, the optimal membrane material would have a negative charge. Choo et al. (2000) observed higher permeate fluxes when the membrane was hydrophilic as opposed to hydrophobic. Hu and Stuckey (2006) was able to maintain higher fluxes with a hollow-fiber membrane than a flat-sheet membrane. In addition, hollow-fibers have a greater surface-area-to-volume ratio and thusly require less space than flat sheets so smaller reactor sizes can be used. Literature report that the optimal pore size is between 0.1 and 0.45 µm (Choo and Lee, 1996; Chung et al., 1998; Elmaleh and Abdelmoumni, 1997).

Based upon literature review, the optimal membrane for an AnMBR system would be constructed of organic, hydrophilic, and negatively charged hollow-fibers with a 0.1-0.45 µm pore size (Bérubé et al., 2006).

2.4 Optimal Conditions for Anaerobic Digestion

Due to the biological nature of anaerobic digestion, there are optimal environmental conditions for achieving maximum microbial activity. The most significant common operating parameters that affect anaerobic digestion performance are temperature, pH, and retention time.

2.4.1 Temperature

Shifts in temperature affect reaction rates, including microbial growth and activity, and microbial community distribution. Thus, slight changes in temperature can have a significant effect on digester performance, especially on acidogenesis rates (Chae et al., 2008; Donoso-Bravo et al., 2009). The optimal temperature for anaerobic digestion, in terms of both VFA and methane production, can be found between 30°C and 40°C (Kasali and Senior, 1989). Zhao et al. (2006) observed maximum acetogenesis and acidogenesis rates at 37°C. Jewell (1987) cites that the minimum methanogenic microbial reproduction times of three days occur at 35°C, and that no methanogens have optimal growth temperatures below 20°C, even though stable methanogenesis is possible at psychrophilic temperature as low as 4 – 5°C (Lettinga et al., 2001). Anaerobic digestion at thermophilic temperatures—around 55°C—may yield improved performance over operation at mesophilic temperatures (Cavinato et al., 2013; Kerroum et al., 2013; Khemkhao et al., 2012). However, the additional energy generated must be weighed against the higher heating investment. Thus, 37°C is a suitable temperature to operate a digester if minimal heating is desired. Additionally, the reactor's temperature should not vary more than 0.6 – 1.2°C for stable operation (WPCF, 1987).

Temperature changes have further effects on AnMBR systems. For example, psychrophilic temperatures incur greater membrane fouling rates than mesophilic temperatures due to higher total suspended solids concentrations as a result of reduced microbial activity (Martinez-Sosa et al., 2011). Thermophilic AnMBRs experience less cake formation than their mesophilic counterparts, but can also experience sludge particle size reductions which lead to an overall increase in fouling resistance (Gao et al., 2012; Jeison and van Lier, 2006). Consequently, AnMBRs should be operated under mesophilic conditions to mediate between optimal microbial activity and minimal fouling.

2.4.2 pH

Another parameter that significantly effects anaerobic digestion performance is pH (Gömeç, 2006; Ponsá et al., 2008). pH should be maintained as levels that ensure suitable growth and activity of the microbes that drive the anaerobic digestion process. Dinamarca et al. (2003) observed optimal hydrolysis rates between pH 7 – 8, while studies using a wide range of substrates and feed concentrations have shown that acidogenic and acetogenic bacteria grow and perform optimally between pH 5 – 6 (Bengtsson et al., 2008; Eastman and Ferguson, 1981; Tabatabaei et al., 2011). Methanogens can be found in a wide range of extreme pH conditions (Zinder, 1993), but the majority of methanogens operate in the pH range of 6.3 to 7.8, with optimal performance around pH 7.0 to 7.2 (Bitton, 2010; van Haandel and Lettinga, 1994; B. Zhang et al., 2005).

pH adjustment to optimal process conditions can reduce inhibitory effects, improve microbial growth and activity, and lead to more stable and higher levels of methane production (Liu et al., 2006). Consequently, it is recommended to monitor and control pH to maximize performance. In single-phase systems, a pH around 7.0 is desired to give methanogens the greatest advantage since they can be the most responsive to pH changes. In two-phase systems when pH is uncontrolled, the AP often experiences significant pH drops down to inhibitory or even toxic levels due to the production of VFAs, HCO_3^-, and NH_4^+ (Abubakar and Ismail, 2012; Gomec and Speece, 2003; Jung et al., 2000; Liu et al., 2008). In these extreme situations, pH adjustment should be employed to achieve adequate AD performance.

2.4.3 Hydraulic and Solids Retention Time

Hydraulic retention time (HRT) and solids retention time (SRT) define the amount of time that liquid and solids, respectively, are held within a reactor. Therefore, HRT is equal to the reactor volume divided by the effluent liquid flowrate; SRT is equal to the mass of solids in the reactor divided by the mass flowrate of effluent solids. In conventional anaerobic digesters, HRT and SRT are equivalent since solids are removed along with the liquid effluent. HRT and SRT are important operating parameters since they impact the amount of time available for the microorganisms to work on substrates and grow in the reactor. At too low an HRT and SRT, system performance will suffer as the microorganism process only a minimal amount of material and experience washout. Thus, in deciding a suitable HRT and SRT, the desired microbial

activities and growth rates must be considered. The doubling time for hydrolytic and acidogenic bacteria is between 1 – 1.5 days, for acetogens is between 1 – 4 days, and for methanogens is between 5 – 15 days (Gerardi, 2003). In the start-up of a two-phase AD system, Solera et al. (2002) observed that the number of AP methanogens and non-methanogens decreased considerably when the HRT was 1.7 days versus 4 days. Based on several engineering studies, Ferry (1993) suggests a MP HRT no less than 10 days in order to achieve efficient and stable operation.

One benefit of AnMBR systems is the independent control of HRT and SRT. Since an AnMBR's membrane filters solids out of the liquid effluent and retains the solids in the digester, the HRT can be made higher than the SRT. This allows AnMBR systems to process greater volumes of liquid while achieving comparable or better performance than conventional digesters. For example, Ersu et al. (2010) achieved >93% SCOD removal and >98% nitrification at a 10 – 75 day SRT and 2 hour HRT. Miron et al. (2000) observed the minimum SRT to achieve significant methanogenesis was 8 days when treating domestic sewage sludge. In AnMBRs, HRT and SRT have additional effects on membrane fouling. Huang et al. (2011) observed that at a longer HRT (12 h), membrane fouling was caused by surface modifications from soluble organic compounds, and biomass deposition. At shorter HRTs (10 or 8 h), infinite SRT resulted in a higher suspended solids concentration, which induced faster membrane fouling. Longer SRTs caused higher soluble organics production, which induced more membrane pore blocking and enhanced biofilm development, and thereby resulted in accelerated fouling development. Miron et al. (2000) observed that sludge filterability was greater for sludge under methanogenic than acidogenic conditions, and increased significantly for SRTs greater than 8 – 10 days. An AnMBR system's HRTs and SRTs should be selected to minimize membrane fouling while maximizing microbial activity and treatment performance.

CHAPTER 3

LITERATURE REVIEW FOR HYDROTHERMAL CATALYTIC GASIFICATION

3.1 Overview of Hydrothermal Catalytic Gasification

Hydrothermal catalytic gasification (HCG) is the thermochemical process by which organic matter and a catalytic material are heated and pressurized under conditions that prevent water from entering the gas phase. The organic molecules then react with the catalyst and are converted into methane, carbon dioxide, and hydrogen gas. In the context of this text, 'HCG' shall refer only to subcritical reactions—below the supercritical water temperature of 374°C—unless explicitly stated otherwise. In some other texts, the term HCG may also include supercritical reactions, above 374°C. HCG can also be performed in liquid mediums other than water, but this text shall only refer to experiments conducted with water as the medium.

Compared to anaerobic digestion, effective HCG systems can use high feedstock solids concentrations and can generally achieve significantly higher conversion rates and efficiencies. However, they require higher operating temperatures, more specialized equipment, catalyst inputs, and may be more complex to operate than alternative biogas conversion systems, e.g. anaerobic digesters. Current research on HCG focuses predominantly on the energy yields obtained from processing various feedstocks with different catalysts under a range of operating conditions, along with catalyst development to increase activity and reduce fouling. Table 3.1 presents several examples of HCG conversion systems, which show generally high conversion efficiencies and high energy yields. As may be evident from the Table, carbon gasification and energy yields vary with feedstock, catalyst, catalyst support material, temperature, retention time, and volume fraction of the liquid reaction medium (Azadi et al., 2009; Elliott, 2008).

Table 3.1 Summary of Subcritical and Supercritical HCG Yields with Different Feedstocks and Catalysts

Feedstock	Catalyst	Feed:Catalyst Mass Ratio	Reaction Temp (°C)	Time (min)	Carbon Gasification (mol C-gas / mol C-feed)	Energy Yield (kJ/g-feed)	Reference
Glucose	0.5% Pt/Al_2O_3	0.32	330	30	0.67	---	(Hashaikeh et al., 2005)
Glucose	3% Pt/Al_2O_3	0.19	265	1440	0.84	---	(Cortright et al., 2002)
Lignin	5% Pd/C	0.54	400	15	0.29	---	(Osada et al., 2006a)
Algae (*Chlorella vulgaris*)	Ni wire	1.43	600	2	0.24	---	(Chakinala et al., 2010)
Cellulose	Ni-3288	2.50	350	60	0.84	---	(Minowa and Ogi, 1998)
Wood Flour	Ni/Na	---	350	60	0.42	---	(Elliott, 2008)
Sawdust	Ra-Ni 2800	2.00	303	41	0.29	8.33	(Waldner and Vogel, 2005)
Sawdust	Ra-Ni 2800	1.90	405	25	0.96	16.68	(Waldner and Vogel, 2005)
Activated Sludge	Ra-Ni 4200	1.33	380	30	0.69	8.60	(Afif et al., 2011)
Glucose	Ra-Ni 4200	2.00	350	15	0.51	6.50	(Azadi et al., 2009)
Glycerol	Ra-NiSn	---	225	37	0.86	---	(Huber et al., 2003)
Dairy Manure	Ru	---	355	60	0.99	18.92	(Elliott et al., 2004)
Dried Distillers Grains with Solubles	Ru	---	350	60	1.00	16.28	(Elliott et al., 2004)
Cellulose	5% $Ru/\gamma\text{-}Al_2O_3$	1.67	380	60	0.53	14.17	(Azadi et al., 2012)
Cellulose	5% Ru/C	1.67	380	60	0.72	9.85	(Azadi et al., 2012)
Sawdust	5% $Ru/\alpha\text{-}Al_2O_3$	1.00	550	10	0.99	9.77	(Onwudili and Williams, 2013)
Bagasse	5% Ru/C	0.64	400	30	1.00	13.32	(Osada et al., 2012)
Bagasse	2% Ru/TiO_2	0.26	400	30	0.95	13.13	(Osada et al., 2012)
Algae (*Spirulina platensis*)	2% Ru/C	1.11	400	61	0.37	---	(Stucki et al., 2009)
Algae (*Nannochloropsis sp.*)	5% Ru/C	1.00	410	40	0.27	4.06	(Guan et al., 2012)

As alluded to earlier, HCG can be performed at either subcritical or supercritical temperatures. Supercritical HCG processes generally have higher conversion efficiencies and yields as a result of faster hydrolysis rates and supercritical water reactions. At extremely high temperatures, i.e. 450 – 800 °C, gasification can be performed without a catalyst. However, a catalyst will still act to increase reaction rates at these temperatures. Subcritical HCG's slower hydrolysis rates make it harder to gasify high molecular weight compounds such as lignin, and may require greater quantities of the catalyst, which can be costly. Nevertheless, it can be advantageous to perform HCG at subcritical temperatures since the thermal energy input requirements would be significantly lower (Osada et al., 2006b; Sasaki et al., 2004). Another crucial decision in designing an HCG system is catalyst selection, which will heavily influence the system's conversion performance.

3.2 HCG Catalyst Selection and Preparation

HCG catalysts come in many different forms and can be deployed in a variety of configurations. The physicochemical properties (surface area, porosity, acidity, composition, density), catalytic properties (activity, selectivity, stability), and morphological and mechanical properties (size, shape, strength) of HCG catalysts largely affect gas yields and the distribution of products. HCG catalysts are grouped as either being homogenous or heterogeneous. Homogenous HCG catalysts are soluble alkalis such as NaOH, KOH, $Ca(OH)_2$, Na_2CO_3, K_2CO_3, and $NaHCO_3$. These catalysts hydrolyze particulate organic matter into simple sugars, amino acids, and fatty acids. The simple sugars, and amino acids and fatty acids to a lesser extent, react with the catalysts further and are gasified into primarily hydrogen and carbon dioxide. H_2O_2 can be added alongside homogenous catalysts to increase hydrogen and methane yields through partial oxidation reactions involving the organic substrate, as shown by Equation (3.1), although alone it yields significantly lower hydrogen and methane than with NaOH (Muangrat et al., 2010a). Despite the relatively low cost of homogenous catalysts, heterogeneous catalysts are more commonly employed for HCG reactions in order to achieve higher and faster gas conversion rates.

$$C_nH_m + \frac{n}{2}H_2O_2 \rightarrow n\,CO + \frac{m+n}{2}H_2 \tag{3.1}$$

Heterogeneous HCG catalysts are metal hydrogenation catalysts, of which the most commonly employed are Raney nickel, Ruthenium (Ru), Platinum (Pt), and Palladium (Pd). Raney nickel and Ru are the most popular HCG catalysts owing to their high effectiveness and low costs relative to Pt and Pd. Ru-type catalysts generally achieve the highest carbon gasification and energy yields per unit weight of catalyst and have comparably longer lifetimes, whereas Raney-nickel-type catalysts are at least three times less expensive than other heterogeneous HCG catalysts while being almost as, or even more, effective. Heterogeneous catalysts can be supported on activated carbon, alumina, TiO_2, Ni, or other compounds to enhance catalyst stability. Added supports can have a strong positive or negative effect on gas yield, which varies with each catalyst-support combination (Minowa and Inoue, 1999).

Heterogeneous catalysts can be supplied in several forms: powdered, pelletized, or meshed. Powdered catalysts have the smallest particle size and therefore the highest surface area per unit volume. Hence, the highest activity can be achieved with powdered catalysts, but because of their small size they are prone to being washed out with the effluent water. The larger-sized pelletized catalysts are easier to retain in the system, but are prone to sintering. In experiments by Minowa and Ogi (1998), total catalyst surface area showed little effect on gas yield while smaller catalyst particle sizes led to increased gas yields, which indicates that only the external surface contributes to gasification. Thus, sintering will generally decrease gas production. However, in HCG experiments performed by Baker et al. (1989) at 350°C with pelletized Ni catalyst, the pellets sintered into a single mass which interestingly resulted in little or no loss in catalytic activity. This may be because the catalyst loading was great enough such that maximum gas conversion was being achieved. Sintering may be an issue with lower catalyst loads and smaller particle sizes. Wire mesh catalysts are the easiest to retain inside the reactor because of their large scaffolding body. Due to this design, however, they may be unable to provide sufficient surface area (Azadi and Farnood, 2011).

The method of catalyst preparation will also affect the catalyst's activity. The most significant preparation parameters are temperature, retention time, and environment. Lee et al. (2000) noticed that higher reduction temperatures created Ra-Ni that generated higher gas yields and produced greater amounts of hydrogen and carbon monoxide. This result indicates that the oxidation state of the nickel catalyst is a major factor in the gasification of biomass. HCG metal catalysts can also be reduced with hydrogen gas prior to use in order to increase the amount of

hydrogen available for methanation. Heterogeneous catalysts can also be impregnated with alkali metals. Up to a maximum loading rate, impregnating a nickel catalyst with different alkali carbonates has been shown to increase gas production in order of decreasing atomic weight, or increasing solubility (Lee et al., 2000). However, over-impregnating the heterogeneous catalyst can lead to decreased gas yields.

Mixtures of homogeneous and heterogeneous catalysts provide the possibility of synergistic reactions. In a study by Lee et al. (2000), gasification of rice straw with a Ni/Kieselguhr and Na_2CO_3 catalyst mixture at 300°C for 30 minutes produced higher gas yields than with just Na_2CO_3 catalyst, which also reduced char and oil formation. Increasing the Na_2CO_3/nickel ratio up to 1 sharply increased gas formation by the breakdown of char. Gas conversions were achieved with other alkali catalysts in the following order, from highest to lowest: $Na_2CO_3 > K_2CO_3 > Cs_2CO_3 > Li_2CO_3 > NaHCO_3 > Na_2SO_4 > NaOH$. These results indicate that pH is not the driving factor in enhancing gas yields, as NaOH is a stronger base than several of the other compounds higher on the list. Some catalyst mixtures may be less effective than one of its components alone. For example, using sodium carbonate as a co-catalyst to reduced nickel resulted in higher carbon deposition at supercritical conditions (Roy et al., 2009). It was speculated that precipitation of the dissolved sodium in supercritical water hindered catalyst activity.

3.2.1 Raney-Nickel catalyst

Raney-Nickel (Ra-Ni) is an extremely porous nickel material with reversibly and non-reversibly adsorbed hydrogen that is commonly employed as a catalyst for hydrogenation reactions. Industrial applications of Ra-Ni include the production of nylon and margarine. In many circumstances, hydrogenation and conversion efficiencies with Ra-Ni are comparable to those of more expensive metal catalysts such as ruthenium and platinum (Nishimura, 2001). Due to the high volume of hydrogen gas adsorbed on the nickel surface and contained inside pores, Ra-Ni is pyrophoric—spontaneously combustible in the open atmosphere. Thus, Ra-Ni is stored submerged in a liquid medium, commonly in either water or ethanol, because of this property.

Ra-Ni is synthesized from the leaching of Al from an Al/Ni alloy using NaOH. There are numerous methods for preparing Raney-nickel, each having subtle procedural differences such as with or without hydrogen gas treatment, and storage of the catalyst in ethanol or water. The particular preparation method and conditions affect the catalytic activity of Ra-Ni. The reagent

materials also influence the activity of the resulting Ra-Ni. Fouilloux (1983) produced Ra-Ni with higher specific surface area when the starting Al/Ni material had higher metallic Al content. Furthermore, maximum activity was found with incomplete leaching of aluminum (Spencer and Twigg, 2005), and faster aluminum leaching results in larger Ra-Ni surface area and the formation of small micropores (Tanaka et al., 2000). The leached Al forms sodium aluminate at high NaOH concentrations and aluminum hydroxide at low NaOH concentrations. Aluminum hydroxide can act as a structural promoter for Ra-Ni. Structural supports, such as silica, can increase Ra-Ni activity and lifetime by stabilizing the pore structure (Takenaka et al., 2001).

Literature have established Ra-Ni to be an effective catalyst for the HCG of biomass, with high carbon gasification efficiencies (Elliott, 2008; Veijola and Harkonen, 1975). For example, Afif et al. (2011) achieved 69% carbon gasification efficiency in the HCG of activated sludge, at a 1.8 g Ra-Ni/g dry sludge. Waldner and Vogel (2005) gasified wood forestry residues with Ra-Ni at 400°C and observed >80% carbon conversion efficiencies and found that feed concentrations below 30% avoided char and tar formation while leaving a low organics concentration in the aqueous product. However, like all metal catalysts, Ra-Ni is susceptible to loses in activity with repeated use. The primary modes of Ra-Ni activity loss are solids deposition on the catalyst surface—fouling and coking—, deep pore blockage, poisoning—especially by elemental sulfur—, sintering, and loss of adsorbed hydrogen (Donnot et al., 1991; Spencer and Twigg, 2005). Sintering and deep pore blockage are generally considered to be irreversible, while poisoning and surface deposition can be partially recoverable by mechanical or chemical cleaning. Sintered Ra-Ni can be mechanically milled or pulverized to reproduce the original Ra-Ni particle size; however, because of pore collapse during the sintering process, the produced particles may have up to 100 times less total surface area than the original Ra-Ni particles. Loss of adsorbed hydrogen can be overcome by the external supply of hydrogen gas, as is done with industrial margarine production. For an HCG process, additional hydrogen can be supplied by hydrogen evolution from the HCG reactions.

3.3 HCG Reactions

Based upon the catalyst employed, there are numerous reactions that can contribute to the HCG process. The mechanisms by which gas and other by-products are produced, influencing the gas composition and liquid effluent quality, are dependent upon whether the HCG catalyst is homogeneous or heterogeneous. Homogeneous catalysts break down large carbohydrate molecules into simple sugars through hydrolysis, while heterogeneous catalysts do so by catalytic cracking and hydrogenation through the Horiuti-Polanyi mechanism. Both catalyst types then gasify the simple sugars into hydrogen gas and carbon dioxide. In the presence of a heterogeneous catalyst, the hydrogen gas and carbon dioxide undergo the Sabatier reaction to generate methane. Thus, homogeneous catalysts tend to produce a hydrogen-rich gas while heterogeneous catalysts produce a gas that is richer in methane. Homogeneous catalysts will also inhibit the formation of char and gas from the oil product.

Different feedstock-catalyst combinations also have different reaction kinetics. In water, cellulose breakdown begins at 240°C, above which oil, gases, and char begin to form. In the presence of 1g sodium carbonate per 20g cellulose, cellulose breakdown started at temperatures lower than 180°C, and gas yields doubled (Minowa and Ogi, 1998). In contrast, with 1g of reduced nickel catalyst per 2g cellulose, significant cellulose breakdown did not occur below 260°C, but gas yields were at least 6 times greater than the control.

In addition to the interactions between the feedstock and catalyst, steam reforming and water-gas shift reactions also proceed to produce hydrogen gas (Bridgwater, 2008). When heterogeneous catalysts are used, these water-based reactions can contribute some of the hydrogen gas for methanation. With certain metal catalysts (e.g. Raney Ni and Ru), the Sabatier reaction may take place to beneficially remove carbon dioxide from the gas product and generate additional methane. Figure 3.1 presents a generalized overall model of the HCG reactions.

Table 3.2 HCG Decomposition of Organic Compounds

$C_6H_{12}O_6 + 6H_2O \rightarrow 12H_2 + 6CO_2$	(Hashaikeh et al., 2005)
$C_wH_xO_yN_z + (2w - y)H_2O \rightarrow \left(2w + \frac{x}{2} - y\right)H_2 + wCO_2 + \frac{z}{2}N_2$	(Li et al., 2008)
$C_6H_5OH + nNi \rightarrow C_6H_x\text{-}nNi + (2 - x)H_2 + H_2O$	(Sharma et al., 2006)
$Ni + H_2O \rightarrow NiO + H_2$	(Sharma et al., 2006)
$C_6H_x\text{-}nNi + 6NiO \rightarrow 6CO + (x/2)H_2 + (6 + n)Ni$	(Sharma et al., 2006)

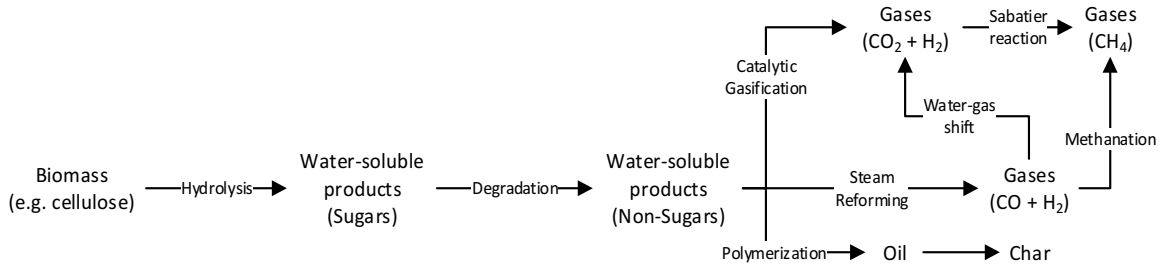

Figure 3.1 HCG Reaction Model, partially adapted from Minowa and Inoue (1999)

Table 3.3 General HCG Reactions

Steam reforming	$C_nH_m + n\,H_2O \rightarrow (n + m/2)\,H_2 + n\,CO$ $CH_nO_m + (1-m)H_2O \rightarrow CO + (n/2 + 1 - m)H_2$
Methanation	$CO + 3H_2 \rightarrow CH_4 + H_2O$
Water-gas shift	$CO + H_2O \rightarrow CO_2 + H_2$
Sabatier reaction	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

As with typical reaction kinetics, higher reaction temperatures and longer reaction times, up to a limit, increases gas yields while maintaining methane quality (Azadi et al., 2009). Higher reaction temperatures increase the rate of reaction while longer reaction times allow more time for the feedstock to be decomposed.

3.4 Reactor Design

The catalytic reactor's design is another notable feature that affects HCG efficiency. The most widely used catalytic reactor designs are plug flow, packed beds, and fluidized beds. Plug flow reactors place the catalyst along the length of a tube, and have the feedstock flow through the tubing over the catalyst. They have a high volumetric conversion and it is possible to pack multiple reactors together to improve heat transfer, but the temperature is hard to control since there will be a temperature gradient along the length of the reactor. The temperature gradient prevents optimal reaction conditions. Packed bed reactors pack the catalyst on the bottoms of a reaction vessel. They have a higher conversion rate and can allow for greater catalyst surface area exposure. Although there is still a temperature gradient along the reactor, the temperature is uniform at the catalyst interface. Nevertheless, surface area is still limited and possible catalyst sintering may be detrimental to the process. Fluidized bed reactors mix the catalyst with the working fluid in the reaction vessel. As a result, fluidized bed reactors have the highest

conversion rates and catalyst surface area exposure. With constant mixing, the temperature remains uniform. The disadvantages of fluidized beds include possible catalyst loss with the liquid effluent, and increased pumping requirements.

CHAPTER 4

OBJECTIVES

4.1 AnMBR Treatment of Municipal Wastewater - Objective and Goals

The primary objective of this portion of the study is to demonstrate a submerged anaerobic membrane bioreactor (AnMBR) system for treating concentrated municipal wastewater biosolids and to evaluate the effects of acid-phase bioaugmentation in a two-phase AnMBR system. In order to accomplish this objective, the following goals were established:

(1) Compare the AnMBR system's start-up time to that of other AnMBR and conventional anaerobic digestion systems.

(2) Assess the non-bioaugmented AnMBR system's steady-state performance based upon the criteria of overall COD reduction, solubilization of COD and VFA production the acid phase, and methane yield.

(3) Evaluate the effects of routine bioaugmentation on the AnMBR system by comparing steady-state performance before and after starting bioaugmentation.

4.2 HCG of Lignocellulosic Waste Biomass – Objective and Goals

The primary objective of this portion of the study is to evaluate the HCG of a common lignocellulosic waste material (i.e. newspaper). The following goals were set to accomplish the objective.

(1) Test HCG of newspaper using a variety of catalysts and compare their carbon conversion and energy yield. The most effective catalyst will then be selected for further study.

(2) Evaluate the selected catalyst's lifetime by performing consecutive HCG tests while reusing the catalyst.

(3) Seek improvements to the HCG process. Novel operation methods and treatments will be investigated to determine their ability to increase performance and lengthen the catalyst's lifetime.

(4) Compare the HCG energy yields to those reported in literature for anaerobic digestion, and perform a net energy comparison between the two processes.

CHAPTER 5
METHODS AND MATERIALS

The following sections and subsections outline the procedures for the anaerobic membrane bioreactor (AnMBR) and hydrothermal catalytic gasification (HCG) experiments.

5.1 Anaerobic Membrane Bioreactor Setup

5.1.1 AnMBR Feedstock

Concentrated municipal wastewater biosolids, pulled from a primary settling tank, was used as feedstock for the AnMBR system. This stream is often called primary sludge and is the first settled fraction of wastewater, which typically contains 30 – 50% of the organics and 60 – 70% of the suspended solids (Tchobanoglous et al., 2003). The dry solids in primary sludge consists mostly of biodegradable organic compounds, followed by a substantial amount of inorganics and a small amount of toxic organics (Kolat and Kadlec, 2013). The organic fraction typically consists of paper fiber, food waste, and fecal matter; the inorganic fraction often contains sand and other miscellaneous grit (ASCE, 2000). The composition of primary sludge can vary greatly from day to day and even hour to hour (Vesilind, 2003).

Primary sludge was obtained from the Urbana Champaign Sanitary District North-East Treatment Facility's primary settling tank. The initial low-strength wastewater feedstock used in this study was made by creating a 1:4 dilution of primary sludge into primary effluent (1:4 primary sludge:primary effluent). The high-strength wastewater feedstock was 100% primary sludge. The chemical properties of the low- and high-strength wastewater are summarized in Table 5.1.

Table 5.1 Chemical Properties of AnMBR Wastewater Feedstock

	Low-strength wastewater	High-strength wastewater
TCOD (mg/L)	8,071 ± 920	44,508 ± 3841
SCOD (mg/L)	763 ± 143	4,778 ± 677
TS (g/L)	4.38 ± 0.073	34.2 ± 1.0
VS (g/L)	3.88 ± 0.068	28.8 ± 0.76
TSS (mg/L)	3,667 ± 76	—
TDS* (mg/L)	711	—
%TS Carbon	42.32	45.28 ± 0.14
%TS Hydrogen	6.08	6.53 ± 0.07
%TS Nitrogen	3.67	2.94 ± 0.10
%TS Oxygen*	47.93	45.26 ± 0.24
pH	7.24 ± 0.02	5.41 ± 0.18
Ammonia (mg/L)	56 ±1	184 ± 56.8

5.1.2 Bioaugmentation Bioculture

Based upon the results of batch experiments to find the most effective bioculture, the final bioculture used on the acid-phase consisted of roughly half anaerobic sludge (recycled from the methane-phase reactor) and half of a blend of proprietary dry biocultures, on a VS basis. The dry bioculture blend was a 1:1:1 VS mixture of proprietary citrus-, hog manure-, and cellulosic-based biocultures obtained from Phylein Inc. Each of the three proprietary biocultures contained 5 – 10 facultative bacterial species that had shown improved acid production in lab experiments. The final bioculture mixture was used for routine bioaugmentation, entailing daily additions to the acid-phase reactor.

5.1.3 AnMBR System Design and Setup

The continuous pilot AnMBR system was set up as a two-phase anaerobic digestion system with separate acid-phase and methane-phase tanks, which provides improved control and optimization of both processes (Hernandez and Edyvean, 2011). The acid-phase (AP) reactor was seeded with a 1:4 mixture of primary sludge and primary effluent, respectively, from the Urbana-Champaign Sanitary District North-East Treatment Facility's (UCSD) primary settling tank. The methane-phase (MP) reactor was seeded with anaerobic sludge from the UCSD's primary anaerobic digester. Figure 5.1 below shows the two-phase pilot AnMBR system schematic, while Figure 5.2 shows the actual physical setup at UIUC.

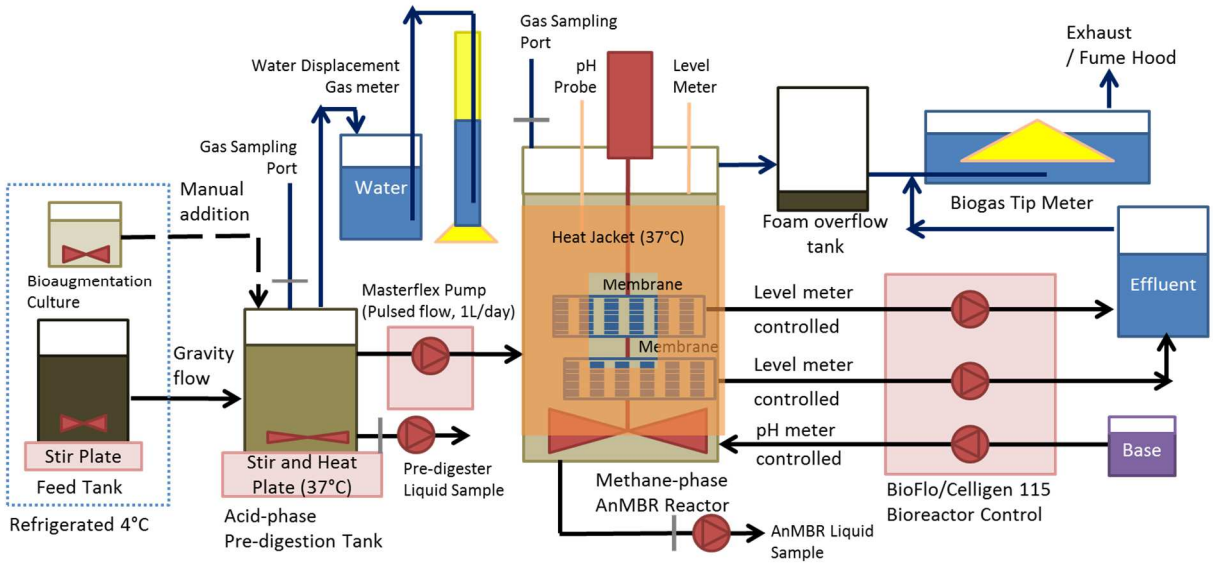

Figure 5.1 Continuous AnMBR System Schematic

A Python software script was written to command a Labjack U3 DAC that controls a Masterflex LS 07523-40 pump to semi-continuously pump liquid from the 2.5L gastight AP reactor to the gastight MP reactor. The continuously stirred AP pre-digestion tank was maintained at 37 ± 2˚C and automatically refills to its preset liquid volume by gravity flow from the refrigerated 4˚C stirred influent tank, which contains the wastewater feedstock. The MP reactor consists of a 14L New Brunswick BioFlo 115 bioreactor. The BioFlo control unit provides mixing, temperature, pH control, and level control in the MP reactor. Default settings for these operating parameters are 120 RPM, 37˚C and pH 7.5. The Bioflo unit draws the system effluent out through the MP reactor's submerged membranes to maintain the desired liquid level as measured by a liquid level sensor. MP biogas is continuously measured using a gas tip meter. After 131 days of operation, a foam overflow tank was added between the MP reactor and gas meter to mediate the thick foam layer which developed on the MP liquid surface that would occasionally overflow out of the MP reactor. A gas outlet from the effluent tank connects to the gas tip meter to account for any gas that is pulled through the membranes. A valve in the effluent line (not shown) allows for effluent to be backwashed by manual pumping.

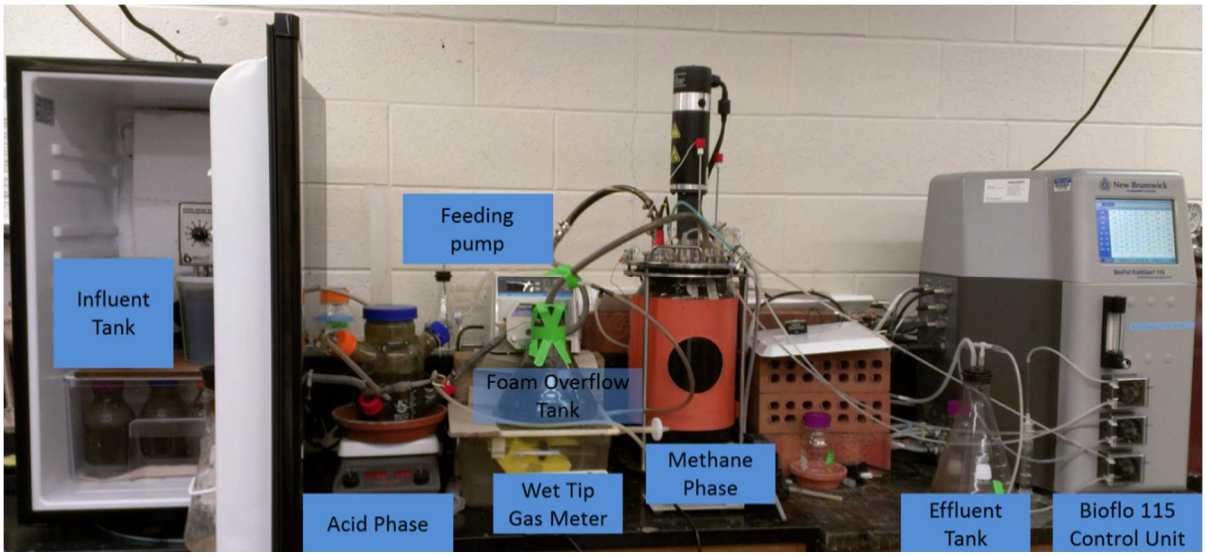

Figure 5.2 Continuous AnMBR System Physical Setup

5.1.3.1 Membrane selection

As discussed in Section 2.3.1, the literature reports that the optimal membrane for an AnMBR system would be constructed of organic, hydrophilic, and negatively charged hollow-fibers with a 0.1 – 0.45 µm pore size (Bérubé et al., 2006; Hai et al., 2005; Kang et al., 2002; Singhania et al., 2012). Consequently, a custom-built 0.2 µm pore size, 0.15 m^2 polyethersulfone hollow-fiber membrane was solicited from Membrana GmbH. While the Membrana membrane was being fabricated, the reactor began operation with a 10 µm pore size, 0.11 m^2 cylindrical Omnifilter RS14-DS sediment filter cartridge. A flux of <5 L m^{-2} h^{-1} was targeted to minimize fouling (Skouteris et al., 2012). The filter cartridge achieved 0.373 L m^{-2} h^{-1} at a flowrate of 1L/day. During this initial period, the filter cartridge was capable of achieving the required effluent flowrate of 1 L/day.

The Membrane membrane was installed on Day 131. The original Membrana membrane module is shown in Figures 5.3A and 5.3B. Within several days of operation, however, the membrane was unable to achieve the required effluent flowrate due to the housing design. Firstly, the holes in the housing were too small such that solids were not released by backwashing, expediting biofouling. Secondly, the housing's sealed top trapped rising biogas, which was pulled through the membrane instead of AnMBR liquid. The Membrana membrane housing was then modified on Day 138 to have larger holes for more effective backwashing, and openings were made at the housing's top to release biogas. Figures 5.3C and 5.3D show the

casing modifications after extended use in the AnMBR reactor. Despite the Membrana membrane's 36% greater surface area, the Sediment filters were able to achieve greater flowrates and fluxes. This may be due to the tight bundling of the Membrana membrane's hollow-fibers, which made the innermost fibers inaccessible after significant biofouling.

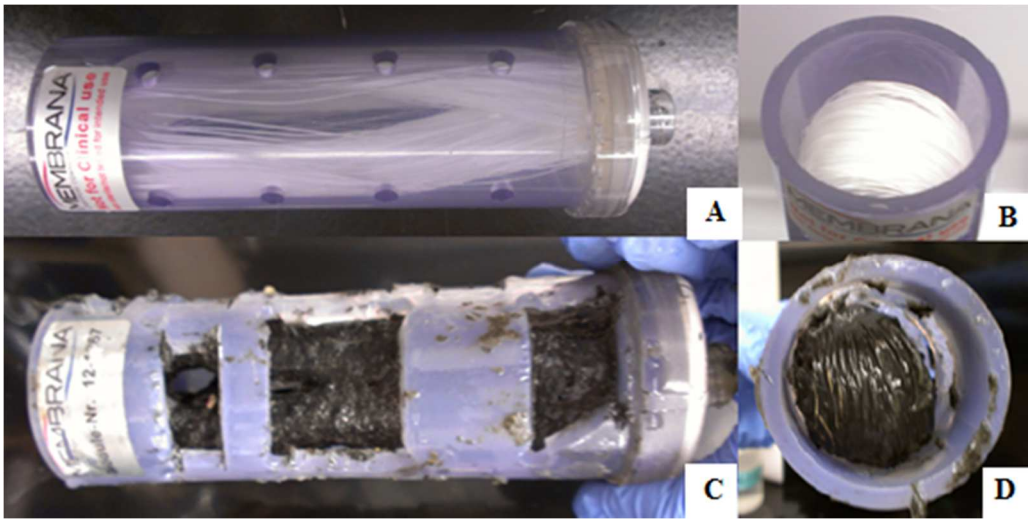

Figure 5.3 Custom-Built Membrana membrane

Due to the Membrana membrane's insufficient flux, the system was switched back to using the filter cartridges. At this time, an extra filter cartridge was added to decrease the loading on a single membrane. On Day 198, the two sediment filters were modified by halving their length and manifolding the cut ends together which allowed for a decrease in AnMBR reactor liquid volume, thereby lowering the AnMBR reactor HRT. The total effective surface area was consequently increased from 0.22 m^2 to 0.258 m^2.

5.1.4 AnMBR Operation

The pre-digestion tank was seeded with the low OLR wastewater, while the AnMBR system was seeded with anaerobic digestion sludge. The system was then operated as a batch process for one week to permit sufficient microbial growth without washout. Operation then transitioned to semi-continuous feeding thereafter.

Table 5.2 Operating Parameters of Continuous AnMBR System

	Low OLR		Medium OLR		High (Variable) OLR	
	Acid-Phase	Methane-Phase	Acid-Phase	Methane-Phase	Acid-Phase	Methane-Phase
Flowrate (L day^{-1})	1	1	0.6	0.6	0.16-1.4	0.16-1.4
Liquid Volume (L)	2	12	1.5	9.5-11	2	12
HRT (days)	2	12	2.5	15-18	1.4-12.5	8.6-75
SRT (days)	2	600	2.5	79-92	1.4-12.5	100
Flux (L m^{-2} hr^{-1})	—	0.373	—	0.159-0.278	—	0.097
Membrane module	—	1 Filter cartridge	—	2 Modified filter cartridges	—	Membrana + Filter cartridge
Influent VS (g L^{-1})	3.38	—	28.76	—	28.76	—
Organic loading rate (g-COD L^{-1} day^{-1})	0.73	—	2.5	—	0.82-7.1	—
Temperature (°C)	37±3	37±1	37±3	37±1	37±3	37±1
pH	5-6	7.5	4.5-5	7.5	4.5-5	7.5
Bioaugmentation	—	—	3.9% by VS	—	1.8% by VS	—

Throughout the course of its operation, the AnMBR system was operated at three long-term organic loading rates. The AnMBR system began operation at the low organic loading rate using a 1:4 mixture of primary sludge and primary effluent, respectively. Operation was later switched to a high organic loading rate by replacing the feedstock with 100% primary sludge. However, operation at the high OLR targeting 5.1 g-COD/L/day induced drastic membrane fouling that resulted in a nearly 4× drop in flux capability. Subsequently, the influent flowrate was lowered to reach the medium OLR condition. As expected, higher flux capability was achieved at the lower OLR. Due to the lower influent flowrate, the pre-digestion and AnMBR HRTs were lengthened. To diminish the rise in HRT, the pre-digestion and AnMBR reactor volumes were lowered. Table 5.2 outlines the operating conditions under the three implemented OLRs.

5.2 Hydrothermal Catalytic Gasification Setup

5.2.1 HCG Feedstock

Newspaper was used as the feedstock for the HCG experiments and was manually shredded into pieces of roughly 0.25 inches in diameter before use. Table 5.3 summarizes the chemical properties and elemental distribution of the newspaper HCG feedstock used.

Table 5.3 Newspaper Chemical Characteristics

	Newspaper
TS (%)	91.74 ± 0.17
VS (%)	91.31 ± 0.32
Carbon (%TS)	49.47 ± 0.02
Hydrogen (%TS)	5.98 ± 0.03
Nitrogen (%TS)	0.31 ± 0.01
Oxygen[a] (%TS)	44.24 ± 0.04

[a] Calculated by difference

5.2.2 Catalyst Preparation

Heterogeneous NaOH catalyst was obtained in the form of ≥97.0% ACS pellets from Sigma-Aldrich. Raney nickel W-5 catalyst was synthesized using 50/50 aluminum-nickel Raney-type alloy powder from Acros Organics and following the method devised by Pavlic and Adkins (1946). Equation (5.1) shows the chemical reaction for Ra-Ni synthesis, an exothermic reaction.

$$2NiAl + 2NaOH + 6H_2O \rightarrow 2(Raney\text{-}Ni) + 2NaAl(OH)_4 + 3H_2 \quad (5.1)$$

Unless noted otherwise, Al/Ni alloy powder was sequentially added to a magnetically stirred 6.667M solution of NaOH in DI water. The reaction environment was maintained at 50°C – 60°C using a combination of hot plate and ice packs. Al/Ni alloy powder was added to the NaOH solution over the course of 1 – 1.5 hours to mitigate temperature and prevent over-foaming from H_2 evolution. After the initial addition period, the alloy was allowed to further digest for another 50 minutes. The liquid reaction medium was decanted into a waste container, and the solid metal catalyst was subsequently rinsed repeatedly under DI water before being extracted. The final catalyst was then stored submerged in DI water and refrigerated at 4°C, typically for use the next day.

5.2.3 HCG Reaction Experiments

HCG reaction experiments were carried out using three Parr 4593 100ml reactors, rated up to 350°C and 5000 psi. Prior to each experiment, the reaction chamber was rinsed with DI water and then dried. The reaction chamber was weighed before and after the experiment. Feedstock was first added to the empty chamber. Raney nickel was then weighed out using the

method prescribed by Gonzalez et al. (2004). For this method, a chosen volume of DI water was poured into a graduated cylinder and weighed [Mass B]. Raney nickel was then added to the graduated cylinder and water was decanted out to retain the previously chosen volume. The graduated cylinder with Raney nickel and DI water was then weighed [Mass A]. The actual weight of Raney nickel added was calculated by Equation (5.2).

$$Ra\text{-}Ni\ mass = 1.167(Mass\ B - Mass\ A) \tag{5.2}$$

1.167 accounts for the volume of water displaced by the Raney nickel catalyst with an average density of 7.00 g/mL. DI water was used to rinse the Ra-Ni out of the graduated cylinder, and added to obtain the desired feedstock moisture content. After sealing the reaction vessels, they were purged with N_2 gas three times and then pressurized to roughly 800 psi. After venting out the gas supply lines, the heating and stirring was turned on. The reactor was heated to the desired setpoint temperature—typically to 345-350°C after one hour of heating—and maintained at the setpoint temperature for the desired reaction time—usually 30 minutes. The reactor temperature and pressure were noted down when the heating began, and then recorded every five minutes thereafter until the end of experiment when the reactor had cooled enough to allow sample collection. The reactor was rapidly cooled to near-ambient temperature before collecting the gas samples into 10L Supel Inert gas sampling bags. Aqueous and solid products were transferred into glass jars and stored at 4°C until analysis.

5.3 Chemical Testing and Analysis

The following subsections outline the methods and procedures for chemical analyses performed on the feedstocks and products.

5.3.1 Aqueous Solution Analysis

Liquid samples were stored at 4°C prior to analysis. COD, pH, ammonia, sulfide, moisture content, and solid contents were measured according to standard methods (Clesceri, 1998). Elemental carbon, hydrogen, and nitrogen (CHN) analysis was conducted by the University of Illinois at Urbana-Champaign Microanalysis Lab using a CHN analyzer (Exeter Analytical, Inc. CE-440). Percent oxygen was calculated based on subtracting the other major

elemental percentages (C, H, and N) from 100%. This calculation neglects all the other minor elements and slightly overestimates the oxygen percentage.

5.3.2 Gas Analysis

Gas composition was analyzed by gas chromatography (Varian, Model 3800), which measured H_2, N_2, O_2, CO, CO_2, and CH_4.

For the HCG experiments, the volume of gas produced was initially calculated by the difference in reactor pressure prior to heating and at the experiment's end. The calculated volumes were occasionally verified by collecting all the gas produced into a 10L Supel Inert gas sampling bag, and then using a graduated glass syringe to manually extract and quantify the gas. Calculated gas quantities only varied from actual measurements by a 1-5% relative standard error. In later tests, the gas produced was solely measured by using a graduated glass syringe to achieve the greatest accuracy.

For the AnMBR experiment, theoretical methane production was estimated based on elemental CHN composition and stoichiometry of anaerobic digestion, as shown by Equation (5.3).

$$C_aH_bO_cN_d + \frac{(4a-b-2c+3d)}{4}H_2O \rightarrow \frac{(4a+b-2c-3d)}{8}CH_4 + \frac{(4a-b+2c+3d)}{8}CO_2 + dNH_3 \quad (5.3)$$

CHAPTER 6

RESULTS AND DISCUSSION

6.1 AnMBR Performance With and Without Bioaugmentation

6.1.1 Start-Up Time

Start-up time is an important factor in the deployment of anaerobic digesters. During this start-up period, the microbial population grows while biomass accumulates in the system, yielding a gradual increase in digester performance. Long start-up times restrict anaerobic digesters from being applied in time-sensitive situations, such as military operations and disaster relief efforts, where stable wastewater treatment and energy production are required at a moment's notice. Longer start-up times also accrue more costs before receiving benefits from the system. Conventional anaerobic digester systems can reach steady-state conditions between 1 – 3 months (Anderson et al., 1994; Huang et al., 2011), but typically take up to 3 months (Deublein and Steinhauser, 2011). However, the retention of biomass in an AnMBR system can potentially shorten the time required for digester start-up (Dereli et al., 2012).

The AnMBR system was operated as a batch process for the first week before switching to semi-continuous feeding. Figure 6.1, Figure 6.2, and Figure 6.3 show the biomass accumulation and methane yield during the start-up of the AnMBR system used in this study. By 4.5 weeks, the acid-phase (AP) reactor achieved a steady level of COD solubilization, with SCOD concentrations around 1000 mg/L (Figure 6.1). Biomass then quickly accumulated during the following 1.5 weeks until reaching a steady-state at 7000 mg/L. This indicates that acclimatization and adaptation of the microbial community took 4.5 weeks in the AP reactor, and that it took an extra 1.5 weeks to achieve the maximum microbial population.

At about 4.5 weeks after starting the system, significant digestion and methanogenesis in the AnMBR reactor was also observed, signified by the sharp drop in MP SCOD concentration and the approach of MP methane yield to the theoretical maximum limit. The days which exceed the theoretical maximum methane production suggest digestion of previously undigested material. During week 5, AP TCOD concentration rises rapidly by 212%, indicating microbial growth in response to acclimatization up to week 4. TCOD concentration then rises by 16%,

14%, and 5% for the following three weeks, respectively, before leveling off at a steady-state-level around 7,000 mg/L.

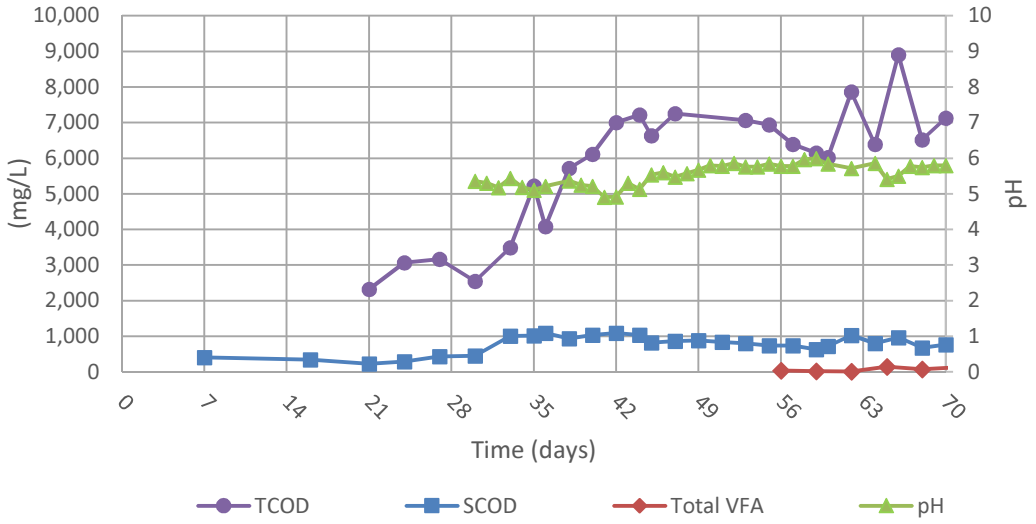

Figure 6.1 Acid-Phase Reactor Organics Concentrations During Start-Up

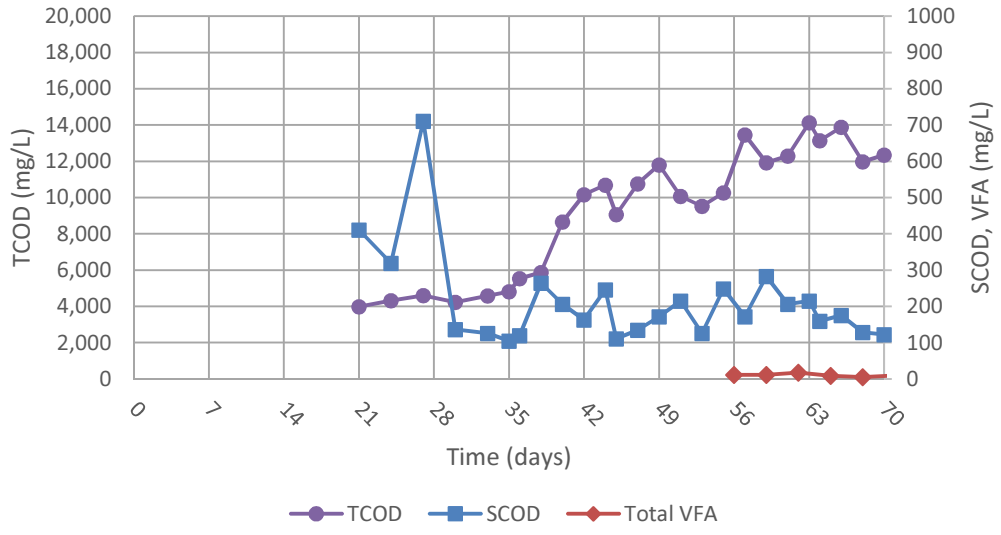

Figure 6.2 Methane-Phase Reactor Organics Concentrations During Start-Up

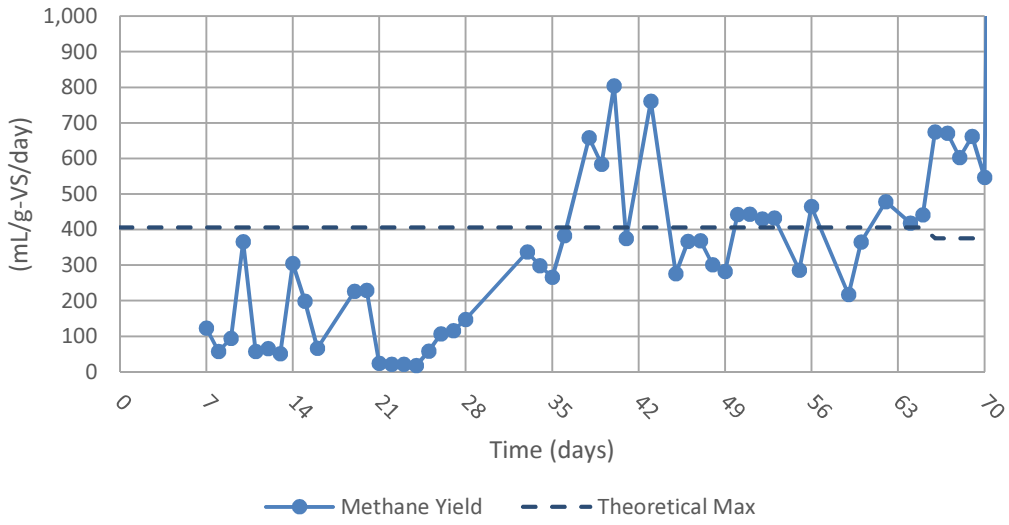

Figure 6.3 Methane-Phase Reactor Methane Yield During Start-Up

To complete the start-up period and reach steady-state conditions, the AP took 6 weeks while the MP took 8 – 9 weeks. However, a high level of microbial activity was already achieved by week 6. The longer start-up time for the MP is attributed to the larger working volume, slow methanogenic growth rates, and the continuous retention of solids and biofilm development on the membrane. For comparison, other AnMBR systems treating synthetic and municipal wastewater took 40 – 80 days to start up (Ho and Sung, 2010; Ince et al., 1997, 1995). Our AnMBR system thus falls within the typical range of AnMBR start-up time.

6.1.2 System COD Removal

One of the main purposes of wastewater treatment is to reduce the concentration of organic compounds. COD, an indirect measurement of organic compounds, was measured throughout the AnMBR system's operation. Figure 6.4 shows the AnMBR system COD removal, calculated as effluent SCOD divided by the feed wastewater TCOD. It should be noted that effluent TCOD and SCOD only differed by 37.5 mg/L on average, while the feed wastewater was 1 – 2 magnitudes greater than effluent SCOD. Furthermore, all commercially available full-scale AnMBR systems use membranes with a smaller pore size that would result in a negligible difference between SCOD and TCOD.

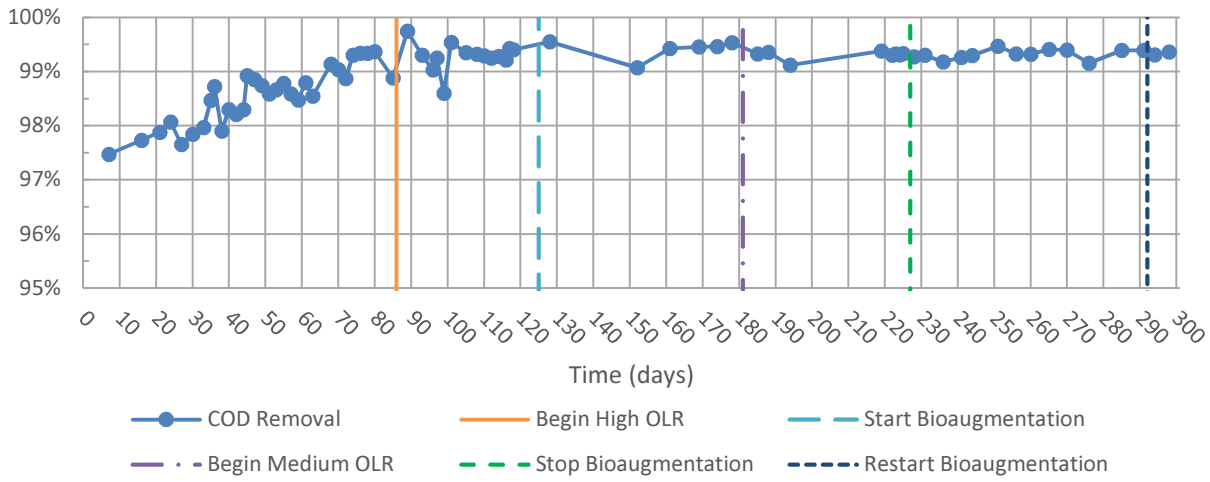

Figure 6.4 AnMBR System COD Removal

Even from the first measurements after starting the AnMBR system, it was already able to accomplish 97.5% COD removal, primarily due to the membrane's physical rejection of solids. After achieving steady-state COD removal on day 74, the AnMBR system was able to consistently achieve >99% TCOD removal. After beginning the high OLR, there was a drop in COD removal to 98.6% and effluent SCOD increased from 80 mg/L to > 400 mg/L as the microbial population needed time to grow in response to the greater influx of organics. However, the high COD removal rate was recovered after 15 days when effluent SCOD dropped down to 300 mg/L. Neither the addition of bioculture nor the reduction in OLR to the medium OLR reduce COD removal below 99%. Treating municipal wastewater under mesophilic conditions, conventional anaerobic digesters typically achieve around 60% – 70% COD reduction and can achieve up to 90% with upflow anaerobic sludge blankets (Bodík et al., 2000; Fang and Chui, 1994; Kalloum et al., 2011; Singh and Viraraghavan, 1998), but AnMBR systems have been shown to typically achieve around 95% COD reduction at significantly lower HRTs (Bodkhe, 2008; Holler and Trösch, 2001). Our AnMBR system achieved above average COD reduction, which is likely due to the addition of an AP pre-digestion reactor and slightly longer HRTs.

6.1.3 Organics Degradation

Effective organics degradation is important to the overall anaerobic digestion performance, not only governing the removal of organics for wastewater treatment, but also

potentially impacting methane production. Organics degradation has further significance for AnMBR systems in terms of breaking down particulate solids to reduce the concentration of potential membrane foulants. Figure 6.5 shows the time sequence of various measures of the organics concentrations for the influent and AP reactor. Influent TCOD and SCOD are also shown simply to establish that any changes in AP organics concentrations are not caused by the influent. Throughout the use of the high-strength wastewater (HSWW), starting on day 86, influent TCOD and SCOD concentrations remained relatively consistent.

Under the low OLR which used low-strength wastewater (LSWW), AP SCOD concentration—487 mg/L—was slightly less than half that of the influent—900 mg/L—, indicating that AP SCOD consumption rates were higher than the hydrolysis rate. AP SCOD also only constituted 8.5% of the AP TCOD, compared to 10.5% for the influent. Therefore, hydrolysis was the rate-limiting AP step during this stage of the experiments. However, after switching to the HSWW, AP SCOD was more than twice that of the influent (10,000 vs. 4,600 mg/L). In addition, AP SCOD constituted 18 – 25% of AP TCOD, whereas AP Total VFA constituted 25% of AP SCOD. These results suggest that acid-production was the rate-limiting AP step during the HSWW portion of the study.

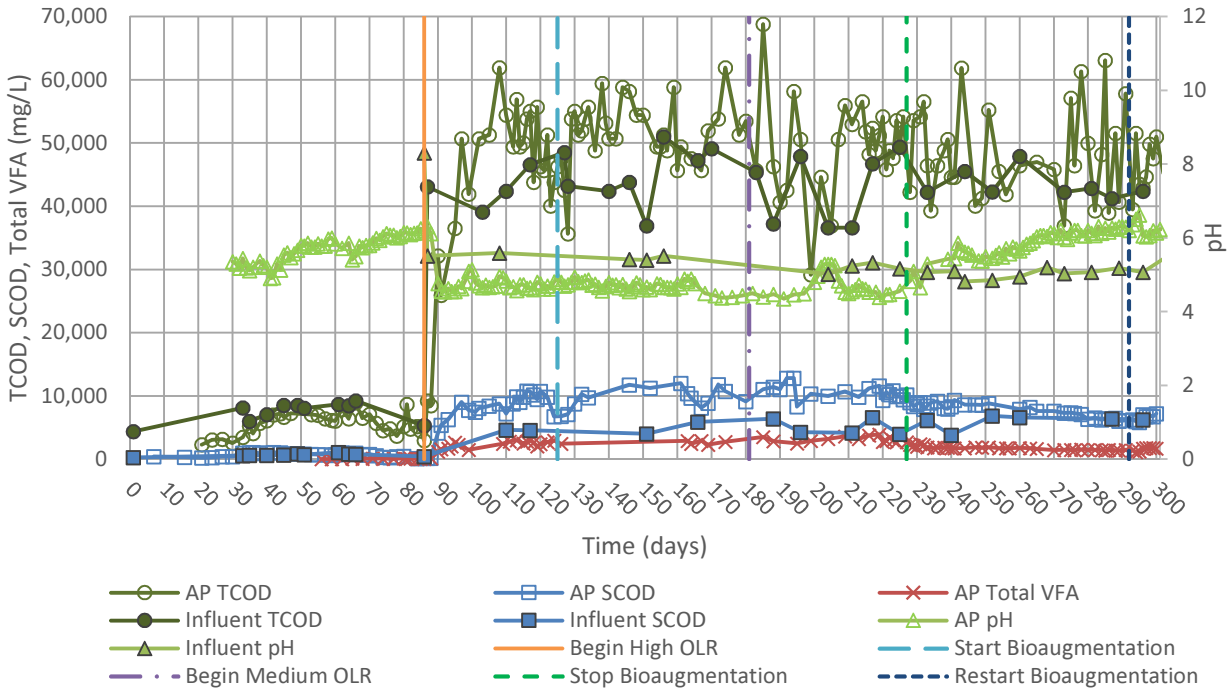

Figure 6.5 Influent and Acid-Phase Organics Concentrations and pH

Routine daily addition of bioculture into the acid-phase (AP) was tested as a potential treatment to improve organics degradation by increasing both the rates of hydrolysis and acid-production. In switching to bioaugmentation at the high OLR, there was no significant change in SCOD production, VFA production, or VFA distribution. This may be attributed to inconsistent feeding, such that the AP and MP HRT without bioaugmentation was 2.3 and 12.6 days, respectively; and 1.5 and 8.5 days with bioaugmentation, respectively. Furthermore, the high OLR with bioaugmentation condition was unable to achieve the setpoint for effluent removal from the MP reactor as a result of significant membrane fouling. These aberrations make it so that the bioaugmentation and non-bioaugmentation conditions under the high OLR cannot be fairly compared. The AnMBR system was subsequently operated at the medium OLR starting on day 181. Under this loading, steady and effective effluent removal was achieved, and the HRTs remained similar with and without bioaugmentation. Thus, the steady-state data under the medium OLR were used to compare to effects of bioaugmentation on reactor performance (Table 6.1).

Under the medium OLR, the bioculture loading consisted of a 1.66% VS dosage of AD sludge bioculture VS dosage and a 2.25% VS loading of dry bioculture blend. When bioaugmenting, the AP reactor pH dropped significantly from 6.2 down to 4.5—even with an influent pH that was slightly higher by 0.2—, suggesting increased acid concentrations and production as the bioaugmentation was designed to provide. Without pH control, Kim et al. (2003) experienced a drastic drop in acid-phase pH due to naturally high VFA formation. Also, AP pH was lower than the influent pH when bioaugmenting, and vice versa when not bioaugmenting (Figure 6.5). Therefore, total acid consumption is likely greater than total acid production when not bioaugmenting, but bioaugmentation increases the rates of acid-production such that production exceeded consumption, which resulted in acid accumulation. To investigate whether this was true, COD and VFA concentrations were measured and analyzed. Without bioaugmentation, total VFA concentration was 126 mg/L lower in the AP than in the influent, while with bioaugmentation, total VFA concentration was 1,478 mg/L higher in the AP than in the influent. This confirms the conclusions implied from the pH differences.

Table 6.1 Steady-State Organics Concentrations at the Medium OLR, With or Without Bioaugmentation

	Without Bioaugmentation Day 227 – 292				With Bioaugmentation Day 181 – 227			
	Influent	AP	MP	Effluent	Influent	AP	MP	Effluent
HRT (d)	—	2.5	18.3	—	—	2.4	15.2	—
pH	5.03 ± 0.04	6.22 ± 0.02	7.57 ± 0.02	7.92 ± 0.03	5.19 ± 0.06	4.50 ± 0.03	7.67 ± 0.02	7.78 ± 0.05
TS (mg/L)	34,827	—	37,643 ± 759	—	33,400	—	41,614 ± 1,031	—
VS (mg/L)	29,253	—	24,439 ± 567	—	28,167	—	25,704 ± 637	—
TCOD (mg/L)	43,843 ± 879	52,196 ± 3,019	39,096 ± 873	292 ± 13	42,404 ± 2,309	49,849 ± 932	42,207 ± 1,302	368 ± 21
SCOD (mg/L)	5,854 ± 603	6,390 ± 60	405 ± 16	295 ± 15	5,091 ± 520	9,946 ± 206	613 ± 17	324 ± 3
VFAs (mg/L)	1,614 ± 20	1,483 ± 25	8.66 ± 0.86	BD	1,656 ± 5	3,134 ± 181	9.55 ± 1.98	BD
Butyrate (mg/L)	345 ± 6	323 ± 8	BD	BD	355 ± 2	475 ± 25	BD	BD
Propionate (mg/L)	552 ± 2	711 ± 5	3.53 ± 0.10	BD	567 ± 2	1,780 ± 137	7.93 ± 1.86	BD
Acetate (mg/L)	717 ± 12	449 ± 12	5.13 ± 0.76	BD	734 ± 1	879 ± 19	1.62 ± 0.12	BD

*Note: '—' indicates no analyzed samples, 'BD' indicates analyzed samples but below detection limit

With bioaugmentation, AP SCOD, butyrate, propionate, and acetate concentrations were higher by 56%, 47%, 150%, and 96%, respectively. This suggests that bioaugmentation improved the rates of all AP reactions. However, these results can be influenced by changes in the influent values, and so it also would be informative to note AP concentration changes with respect to influent values. Without bioaugmentation, the AP increased SCOD by 536 mg/L (9.2%), butyrate remained relatively unchanged, propionate increased by 159 mg/L (28.9%), and acetate decreased by 268 mg/L (37%) with respect to the influent. The accumulation of propionate indicates acetogenesis was a rate-limiting AP step. With bioaugmentation, the AP increased SCOD by 4,855 mg/L (95.4%), butyrate increased by 120 mg/L (33.8%), propionate increased by 1,213 mg/L (214%), and acetate decreased by 145 mg/L (19.8%) with respect to the influent. The differences in AP SCOD and VFA concentrations between samples during and those without bioaugmentation were statistically significant at a > 95% confidence level. Hence, bioaugmentation significantly improved AP organics degradation by increasing the rates of hydrolysis, acidogenesis, and acetogenesis.

Acetogenesis not only remained the rate-limiting step with bioaugmentation, but its relative underperformance was even more pronounced with bioaugmentation as indicated by greater propionate accumulation. The observed propionate accumulation with bioaugmentation was confirmed in batch studies, supporting the fact that acetogenesis was the rate-limiting acid-phase step. It is possible that the acetate concentrations could have caused the accumulation of propionate. Gorris et al. (1989) observed a 60% decrease in propionate degradation when acetate concentrations increased from 100 mg/L to 200 mg/L, while having no effect on butyrate degradation. Our observed acetate concentrations were already 449 mg/L without bioaugmentation, and almost twice that with bioaugmentation. Thus, the feedback mechanism from the buildup of acetate could have inhibited the breakdown of propionate into acetate. This could explain propionate accumulation without bioaugmentation, and even higher propionate accumulation with bioaugmentation.

Effluent COD was under 400 mg/L with bioaugmentation and under 300 mg/L without bioaugmentation. These values are close to regulatory discharge levels, which typically mandate COD concentrations below 125 – 250 mg/L (EPA, 1997), but they would need some further processing in their current form. Recalling that the AD feedstock was the concentrated biosolids from primary sedimentation, the likely route to suitable discharge quality will come from re-mixing AD effluent with the more dilute fraction of wastewater that overflowed from primary sedimentation. Alternatively, adsorbents could be used in the AD process to increase removal of slowly-degrading organic compounds. Finally, effluent from the AnMBR system could be further processed by high pressure nanofiltration or reverse osmosis membranes if very high water quality was desired for certain water reuse applications.

Lower TCOD in the MP than the AP may indicate effective hydrolysis in the MP along with good conversion of SCOD to methane. With and without bioaugmentation, MP SCOD constituted only 1 – 1.5% of MP TCOD. This high reduction of SCOD by the MP suggests non-inhibited methanogenesis. To verify whether the AnMBR system accomplished effective methanogenesis, biogas quality and yields were repeatedly measured.

6.1.4 Methane Production

The primary advantage from anaerobic digestion processes is the production of methane gas for use as biofuel. Methane and carbon dioxide yield were measured in the AP and MP reactors with and without bioaugmentation (

Table 6.2). The hypothesis for this study was that bioaugmentation would increase methane yields by means of enhanced solubilization and acid-production. However, when bioaugmentation was applied to the AP, average methane yield was less and more carbon dioxide was produced in proportion to methane in both the AP and MP. Comparing the AP methane yield with bioaugmentation versus without bioaugmentation indicated a statistically significant difference with a confidence level above 95%. In contrast, the MP methane yield and the total methane yield were not statistically different comparing performance with and without bioaugmentation. Thus, bioaugmentation did not have a clear effect on methane yield. This result contradicts the initial hypothesis and the implications of higher organics degradation with bioaugmentation, which was confirmed to be statistically different. Several possible causes for this were proposed and evaluated:

(1) Small differences in operating conditions resulted in the observed performance. Slightly lower HRT in the MP with bioaugmentation than without bioaugmentation provided in less time for organics destruction and methanogenesis. Lower AP pH inhibited methanogenesis in the AP.

(2) Higher dissolved organics concentration in the MP led to more organics being flushed out in the effluent before being digested

(3) Higher total organics concentration in the MP led to more organics being flushed out by solids removal before being digested

(4) The intermediates of anaerobic digestion (e.g. VFAs) were diverted to alternate and/or less efficient pathways when operating with bioaugmentation

Table 6.2 AnMBR System Methane and Carbon Dioxide Yield, and Sulfide Concentration

	Without Bioaugmentation Day 227 – 292				With Bioaugmentation Day 181 – 227			
	Influent	AP	MP	Effluent	Influent	AP	MP	Effluent
HRT (d)	—	2.5	18.3	—	—	2.4	15.2	—
pH	5.03 ± 0.04	6.22 ± 0.02	7.57 ± 0.02	7.92 ± 0.03	5.19 ± 0.06	4.50 ± 0.03	7.67 ± 0.02	7.78 ± 0.05
Methane yield (ml/gVS-day)	—	22.76 ± 0.44	400.63 ± 7.07	—	—	9.05 ± 0.74	362.60 ± 26.79	—
Carbon dioxide yield (ml/gVS-day)	—	11.14 ± 0.20	158.95 ± 4.09	—	—	15.25 ± 1.62	181.91 ± 16.57	—
S^{2-} (mg/L)	31.65 ± 3.21	31.90 ± 2.29	89.25 ± 1.33	0.03 ± 0.00	25.20 ± 2.24	23.70 ± 1.30	120.96 ± 3.45	0.05 ± 0.01

Addressing the first potential cause—slightly lower HRT when operated with bioaugmentation—bioaugmentation was restarted again after the end of the 'without bioaugmentation' condition on Day 292. Operating at exactly the same HRT and without any changes to the reactor system, increases in AP SCOD and acid production were evident after 3 days of bioaugmentation. Meanwhile, AP and MP methane yield appeared to decrease while carbon dioxide yield increased, producing the same effect as previously observed. Therefore, the difference in HRT was not the reason for lower performance. However, lower methane yields in the AP with bioaugmentation could be explained by the lower pH, since methane content in the AP correlates closely—93.5%—to pH (Figure 6.6).

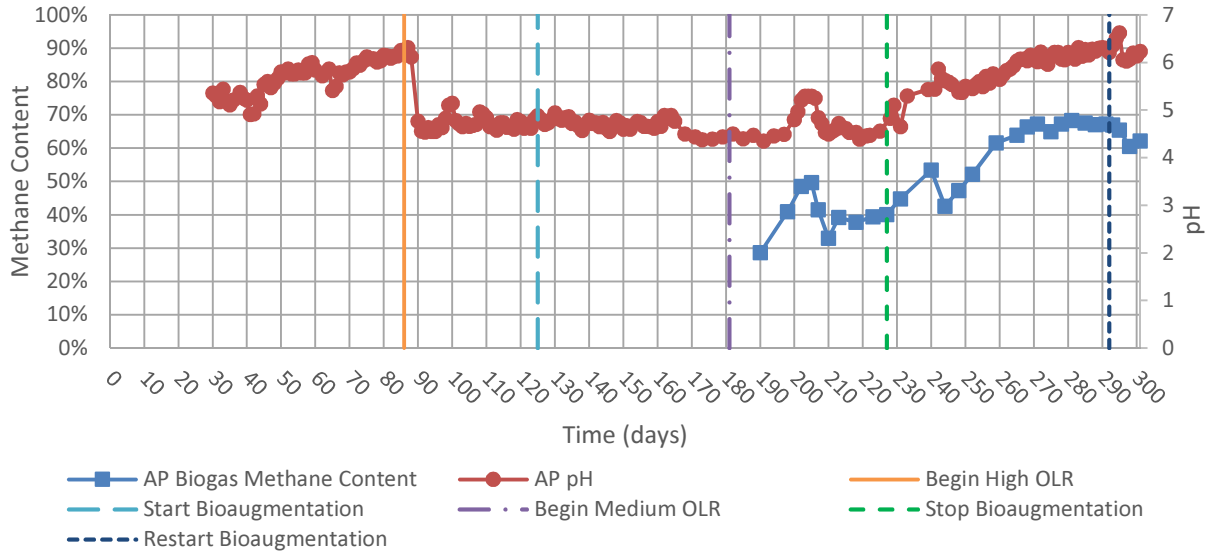

Figure 6.6 Acid-Phase Biogas Methane Content and pH

Since most of the remainder of the biogas is measured to be carbon dioxide, pH must also be highly correlated to carbon dioxide content. It is suspected that increased AP acid-production with bioaugmentation led to low AP pH—4.50 with and 6.22 without bioaugmentation. At lower pH's, less carbon dioxide can dissolve into solution and will thus remain in the gas phase. Also, at such a low pH, methanogenesis would be greatly inhibited. Parawira et al. (2004) had similarly observed that acidic conditions from VFA production inhibited methanogenesis in the AP. However, pH and total VFA concentration were overall -78.8% correlated, with up to -92.3% correlation without bioaugmentation and down to -25.1% correlated without bioaugmentation. Thus, although shifts in VFA concentration can drive changes in pH, it may not have been the sole cause of the pH change observed under bioaugmentation. Higher carbon dioxide production could also drive the pH down by pushing more carbon dioxide into the aqueous phase, as described by Henry's law in Equation (6.1), where p is the partial pressure of CO_2 in the atmosphere, k_H is Henry's constant, and c is the concentration of aqueous CO_2 (i.e. H_2CO_3). Indeed, higher carbon dioxide yield was noted in the AP with bioaugmentation. Consequently, although pH could have had an influence on the AP lower methane yields and higher carbon dioxide yields, another mechanism is needed to simultaneously explain the MP performance where pH was maintained constant.

$$p = k_H c \tag{6.1}$$

The second potential cause was that the higher dissolved organics concentration in the MP when under bioaugmentation led to more organics being flushed out in the effluent before being converted to methane. Referring back to Table 6.1, the effluent TCOD was 368 ± 21 mg/L with bioaugmentation and 292 ± 13 mg/L without bioaugmentation. This accounts for a difference of 45.6 ml of TCOD per day. This amount is negligible compared to the total amount of TCOD added per day—25,000 to 26,000 mg/day. Furthermore, this could not explain the concurrent higher carbon dioxide yield in both reactors. Another possible reason we considered was that higher total organics concentration in the MP led to more organics being flushed out by solids removal before being digested. As the solids flowrate was held steady at 120 ml/day, the difference between the amount of solids removed with and without bioaugmentation would be

373 mg-TCOD/day. This only accounts for 1 – 2 % of the total incoming solids, and again does not account for increased carbon dioxide production.

We then addressed the possibility that organics were being diverted to alternate and/or less efficient pathways when operating with bioaugmentation. Either organics were being used by other organisms not partaking in the anaerobic digestion process, or the microorganisms present in the bioaugmentation culture required more energy to produce the same quantity of products. A common alternative pathway is sulfate reduction. Sulfate reduction is performed by two major groups of sulfate-reducing bacteria—incomplete oxidizers, which reduce large soluble compounds to acetate and CO_2, and complete oxidizers, which convert acetate to CO_2 and HCO_3^-. The sulfurous product of sulfate reduction is hydrogen sulfide, a toxic gas that can corrode metal piping and results in odor issues due to its foul smell. Aqueous sulfide can also react with trace metals in wastewater; the most notable metal sulfide is FeS, which gives the black color to anaerobic sludge.

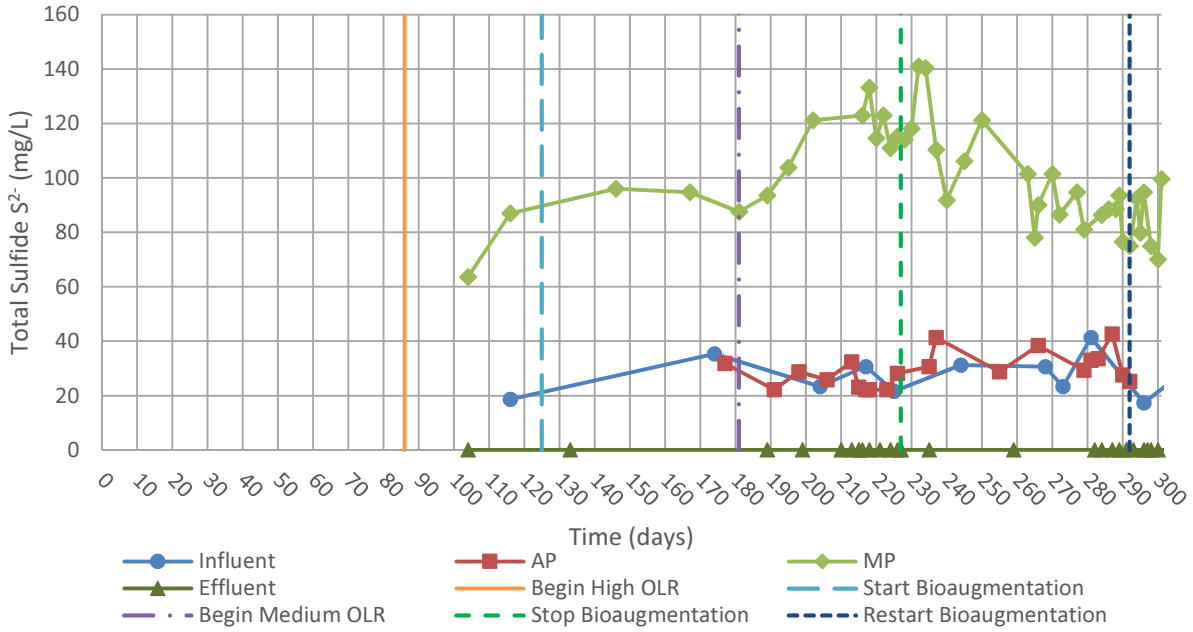

Figure 6.7 AnMBR System Total Sulfide

Total sulfide was thus measured at each stage of the AnMBR system. Total sulfide concentration in the AP was not statistically different from the influent, both with and without bioaugmentation, but MP total sulfide was 2.8x larger without bioaugmentation and 3.8x larger with bioaugmentation compared to the AP (Figure 6.7). This difference came about with no

change in influent total sulfide, indicating greater sulfate reduction under bioaugmentation. The chemical process of sulfate production produces carbon dioxide along with hydrogen sulfide, which can explain the higher carbon dioxide yields with bioaugmentation (Table 6.3). Additionally, sulfate reduction utilizes VFAs which translates to less organics available for methane production, explaining the lower methane yields. Barber and Stuckey (2000) and Harada et al. (1994) observed that increased sulfate reduction led to lower methane yields due to competition for common substrates. It should be noted that the difference in total carbon gasification is not statistically significant with or without bioaugmentation. There was simply a redistribution of carbon, shifting more towards carbon dioxide production when under bioaugmentation. Sulfate-reduction can certainly account for this. The increase in sulfate-reducing activity is suspected to be caused by greater propionate accumulation in the AP from bioaugmentation. The high excess of AP propionate could potentially be consumed by sulfate-reducing bacteria, which have faster reaction rates that are more energetically favorable than acetogenesis. Sulfate-reducers could have also utilized excess acetate. Reis et al. (1991) noted higher sulfate reduction and total sulfide concentrations at higher acetic and propionic acid concentrations. Nevertheless, it is likely that methanogenesis was not inhibited by the increased sulfide production. Khanal and Huang (2005) noted that a dissolved sulfide concentration of 613 mg/L—228 mg/L of free sulfide—would start to impose toxicity on methane-producing bacteria.

On the question of bioaugmentation benefits, the results from this study appear contradictory to previous ones. Bioaugmentation with the same bioculture had shown improved performance in conventional batch and continuous studies treating primary sludge and a variety of other wastes. However, the batch studies can be considered as system start-ups, which can benefit from added bioculture by supplementing microbial growth. In addition, they also were not operated with any membrane, which retains all biosolids in the reactor. The difference with this study's results can be further explained by the high performance already achieved by the two-phase AnMBR system without bioaugmentation. The other continuous systems were not operated with a membrane and naturally had higher organics loss and microbial washout since solids were not retained in the reactor. In these cases, bioaugmentation could increase the amount of solids utilized before being washed out, which does not apply to an AnMBR system.

Table 6.3 Acidogenesis, Methanogenesis and Sulfate-Reducing Reactions, adapted from Stams et al. (2005) and Thauer et al. (1977)

	ΔG^0 (kJ/reaction)
Acidogenic reactions	
$CH_3CH_2COO^- + 3H_2O \rightarrow CH_3COO^- + HCO_3^- + H^+ + 3H_2$	+76.1
$CH_3CH_2COO^- + 2H_2O + 2CO_2 \rightarrow CH_3COO^- + 3HCO_2^- + 3H^+$	+65.3
$CH_3CH_2CH_2COO^- + 2H_2O \rightarrow 2\,CH_3COO^- + H^+ + 2H_2$	+48.3
Homoacidogenic reactions	
$4H_2 + 2HCO_3^- + H^+ \rightarrow CH_3COO^- + 4H_2O$	-104.6
Methanogenic reactions	
$4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O$	-135.6
$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^-$	-31.0
Sulfate-reducing reactions	
$CH_3COO^- + SO_4^{2-} \rightarrow 2HCO_3^- + HS^-$	-47.6
$4CH_3CH_2COO^- + 3SO_4^{2-} \rightarrow 4CH_3COO^- + 4HCO_3^- + 3HS^- + H^+$	-37.7
$2CH_3CH_2CH_2COO^- + SO_4^{2-} \rightarrow 4CH_3COO^- + HS^- + H^+$	-27.8

Koe and Ang (1989) experienced similarly baffling results when bioaugmenting a semi-continuous anaerobic system treating municipal wastewater primary sludge. A 1x and 10x bioaugmentation loading, resulted in lower biogas quality and COD reductions despite higher acetic acid concentrations. In general, bioaugmentation still resulted in higher gas production, except at high feed concentrations where bioaugmentation reduced gas production. However, when the same bioculture was applied to a pilot-scale study, an 8 – 9% increase in biogas production and an 8% decrease in oil and grease in the digested sludge were noted. When the same bioculture was also applied to a full-scale treatment facility, volatile solids destruction increased from 35.5 to 45.1%. Koe and Ang (1989) attributed their observed discrepancy to the fact that their laboratory reactors were already biologically healthy prior to the addition of the bioculture. Further investigation found that the bioculture's bacterial species were not significantly different than the reactors' natural bacterial flora (Koe and Ang, 1992). Tale et al. (2011) observed no significant difference in COD reduction and methane production between

bioaugmented and non-bioaugmented reactors at a 24 day HRT even though performance improved for HRTs ≤ 12 days. When bioaugmenting a continuous two-phase AD system, Nielsen et al. (2007) reported a 9% increase in methane yield although the control (non-bioaugmented) reactor's methane yield increased by 7% at the same time. Cirne et al. (2006) found that *Clostridium lundense* bioaugmented reactors treating restaurant waste had no statistically significant difference in methane yield with the control group already achieving 91 – 98% methanization. The difference was even smaller for a two-stage system. However, bioaugmentation did decrease the start-up time by 30%. These studies support the notion that bioaugmentation may have little, no, or even negative effects when applied to already effective anaerobic digestion processes, and that other operating conditions can have greater influence under these circumstances. After reviewing the results from several full-scale studies and after performing one themselves, McKinney and Poliakoff (1953) asserted that "as long as an activated sludge system is designed and operated according to biological principles, the use of the biocatalysts studied will not increase the efficiency of plant operation." Our current results with a pilot-scale continuous two-phase anaerobic membrane bioreactor system treating municipal wastewater primary sludge concur that bioaugmentation will not improve an AD system that has already naturally achieved high performance. Only during startup or in stressed conditions where performance is degraded would bioaugmentation have an opportunity to improve AD performance. Additionally, bioaugmentation may facilitate operating a reactor at more aggressive OLR conditions, which would save on reactor capital and/or operating costs. In this study, the membrane system did not allow for the system to be operated at a high enough flow rate to achieve more aggressive OLR. However, practical full-scale systems can generally achieve higher membrane flux rates than were achieved in this study, and bioaugmentation would have a better opportunity to provide performance advantages.

6.2 HCG of Newspaper

6.2.1 HCG of Newspaper with Homogenous and Heterogeneous Catalysts

Literature had identified newspaper as a lignocellulosic material that could not be degraded well by conventional anaerobic digestion, and only degraded marginally better with pretreatment. Thus, HCG was tested as an alternative processing method to determine if higher

conversions could be achieved. Raney nickel (Ra-Ni) was selected as one of the catalysts to test due to its low cost and comparable efficiencies compared to other hydrogenation catalysts. W-5 type Ra-Ni was chosen due to its relatively simple synthesis procedure thereby minimizing parasitic costs. 50/50 Al/Ni powder and NaOH, reagents used in the synthesis of Ra-Ni, were also tested to determine their influence on the performance of Ra-Ni. NaOH is also reported as an effective homogenous HCG catalyst. Na_2CO_3 was tested as an alternative homogenous catalyst. Figure 6.8 shows gas and energy yields from the HCG of newspaper at 350°C for 30 minutes with and without the various catalysts.

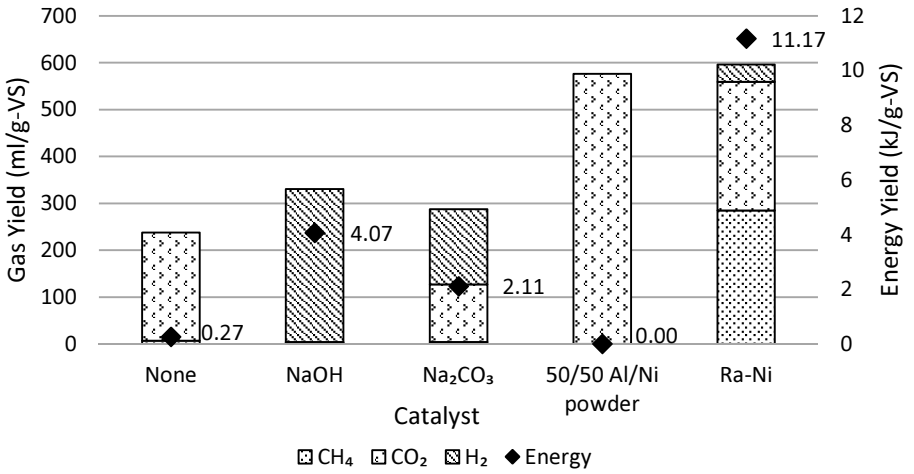

Figure 6.8 Gas and Energy Yields from the HCG of Newspaper
(30 min at 350°C, 86% moisture, 0.92 feed:catalyst ratio for all catalysts except Ra-Ni 1.59 feed:catalyst ratio)
*Feed:catalyst ratio on a dry weight basis

Ra-Ni achieved the highest energy yield (11.17 kJ/g-VS) with 61% carbon gasification despite 42% less catalyst loading than the other alternatives tested. Consequently, Ra-Ni was judged to be the most promising of the tested catalysts, and was chosen for further study. With 42% more loading, 50/50 Al/Ni powder achieved roughly the same carbon conversion as Ra-Ni, but produced only carbon dioxide. HCG with NaOH also produced no methane. This suggests that it is not the presence of nickel or residual NaOH in Ra-Ni that induces methane formation, but rather the presence of adsorbed hydrogen on the catalyst surface. Figure 6.9 physically shows the HCG conversion of newspaper with Ra-Ni. By the end of the HCG process, there was complete degradation of the newspaper particulates into gas and possibly also soluble organics.

It is also evident that the water medium can be readily collected for reuse to minimize the water inputs for continuous processing.

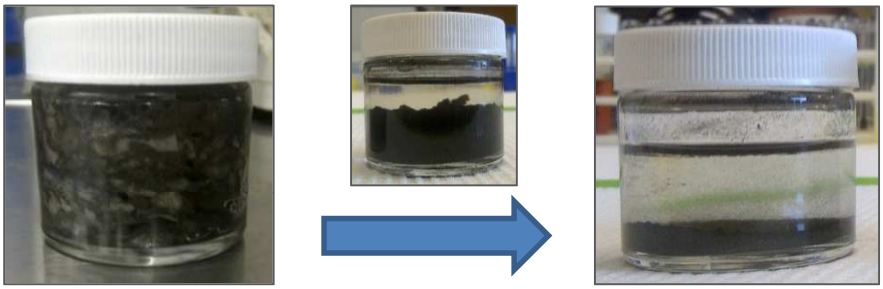

Figure 6.9 HCG with Raney Nickel: Conversion Process
(Left: Before HCG process with Ra-Ni and Newspaper, Middle: During HCG process, Right: End of HCG process with settled Ra-Ni)

HCG with NaOH, attaining the second highest energy yield, is also of interest because of its pure hydrogen gas product. Onwudili and Williams (2009) similarly observed high hydrogen and low methane yield from the HCG of glucose at 350°C. Numerous other studies have also examined the application of NaOH catalyst for HCG-based hydrogen production. Equation (6.2) shows the proposed mechanism by which NaOH promotes the formation of hydrogen gas. Although no carbon dioxide gas was detected, it is unlikely that none of the biomass was converted into carbon dioxide since all other catalysts and even using no catalyst had produced some carbon dioxide. The absence of carbon dioxide in the gas product can be explained by the conversion of carbon dioxide into soluble sodium carbonate, following the same mechanism as that found in CO_2 scrubbers, described by Equation (6.3). This presents the potential for in-situ cleaning of HCG gas.

$$C_6H_{12}O_6 + 6NaOH + 6H_2O \rightarrow 6NaHCO + 12H_2 \quad (6.2)$$

$$2NaOH(aq) + CO_2(g) \rightarrow Na_2CO_3(aq) + H_2O \quad (6.3)$$

6.2.2 Ra-Ni Lifetime Extension with NaOH Co-Catalyst

Given Ra-Ni's high energy yield and carbon conversion achieved, it was chosen for further study of catalyst lifetime. Metal catalysts are known to have efficiency loses over time from fouling (solids deposition and caking), poisoning, sintering, etc. Once catalyst effectiveness falls below economic or process feasibility, replacement or regeneration becomes

necessary. The rate of efficiency loss is therefore an important factor in determining the catalyst's economic viability, indicating how often the catalyst needs replacing and what long-term products distribution and energy yields to expect. Figure 6.10 shows the gas and energy yields from six consecutive rounds of HCG processing newspaper with Ra-Ni. In the first round, Ra-Ni catalyst was added with newspaper feedstock (83% moisture) at a 1.59 feed:catalyst ratio. The same Ra-Ni catalyst was reused for all subsequent rounds, and paper was added each round to match the same 1.59 feed:catalyst ratio. No liquids or solids were removed from the reactor between rounds.

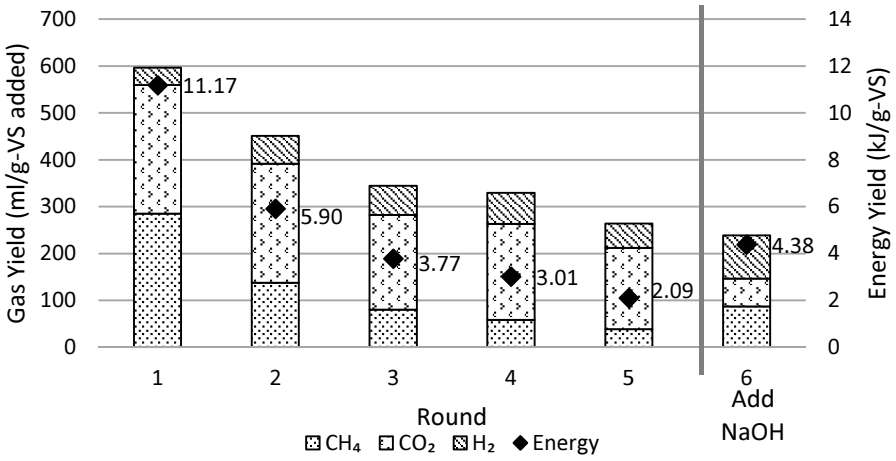

Figure 6.10 Ra-Ni Lifetime and NaOH Regeneration, HCG of Newspaper
(30 min at 350°C, 83% moisture, 1.59 feed:catalyst ratio)

Rounds 1 to 5 show a significant reduction in carbon conversion—86% less methane, and 37% less carbon dioxide—while hydrogen production remains relatively stable. Based on the trend, it is uncertain whether methane and energy production will approach a steady-state value greater than zero. Nevertheless, the best fit exponential and power functions based on least squares estimation indicate that energy yield will fall below 1 kJ/g-VS on run 7 – 12. Assuming a Ra-Ni price of $20/lb (Emerson, 2011) and applying the 2012 average U.S. residential natural gas price of $10.68/($10^3$ ft^3) (US EIA, 2013), 855 runs are required to break even at a constant HCG energy yield of 2.09 kJ/g-VS. Ni/Al_2O_3 catalysts used for industrial methanation have a lifetime of 5 – 10 years while traditional tubular nickel steam reforming catalysts have a typical lifetime of 3 – 5 years — 52,560 – 87,600 rounds (Hagen, 2006; Wagner et al., 2003). However, when hydrogenating complex organic compounds, Ra-Ni lifetime can be as low as 50 – 100

rounds (Shimizu and Suniita, 1975). The current Ra-Ni lifetime is likely to be economically infeasible, demonstrating the need to devise techniques that maintain higher, consistent energy yields. The test on round 6 was an attempt to do just that.

On round 6, NaOH was added alongside newspaper at a 1.83 feed:catalyst ratio. Since NaOH is used in the production of Ra-Ni catalyst and has been shown to be an effective Ra-Ni regenerant (Shimizu and Suniita, 1975), it was proposed that in-situ regeneration of Ra-Ni may be possible by introducing NaOH into the HCG process. Round 6 showed that the addition of NaOH as a co-catalyst improved HCG performance by increasing methane and hydrogen yield while decreasing carbon dioxide gas, either by reactivating Ra-Ni catalyst or through independent side reactions. The addition of NaOH reversed the downward trend of methane and energy yield, instead slightly more than doubling both—38.9 to 86.7 mg/g-VS and 2.09 to 4.38 kJ/g-VS, respectively. The increase in hydrogen yield is probably caused by reactions independent of Ra-Ni, similar to those taking place when NaOH is used as the sole catalyst. Furthermore, akin to HCG with NaOH, the addition of NaOH as a co-catalyst likely scrubbed carbon dioxide from the gas phase, converting it into aqueous sodium carbonate. The solid residues consisted of residual char and ash, which accumulated through each round. At the end of round 6, small white particles were found that were not present in the previous five rounds. The white particles are likely to be precipitated sodium bicarbonate which had formed from further reaction between sodium carbonate with carbon dioxide, as observed by Onwudili and Williams (2007). The mechanism of this reaction is shown by Equation (6.4).

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3 \tag{6.4}$$

Consequently, the addition of NaOH as a co-catalyst provides several immediate benefits to HCG with Ra-Ni. However, to determine whether the addition of NaOH acts to regenerate Ra-Ni and has long-term benefits, a set of consecutive HCG runs with Ra-Ni reuse and NaOH addition in each cycle was conducted. Figure 6.11 shows the gas and energy yields from this experiment. In the first round, Ra-Ni catalyst was added with newspaper feedstock (83% moisture) at a 1.57 feed:catalyst ratio. The same Ra-Ni catalyst was reused for all subsequent rounds, and paper was added each round to match the same 1.57 feed:catalyst ratio. No liquids or solids were removed from the reactor between rounds. NaOH was added on rounds 2 and 3 at a 4.59 feed:catalyst ratio.

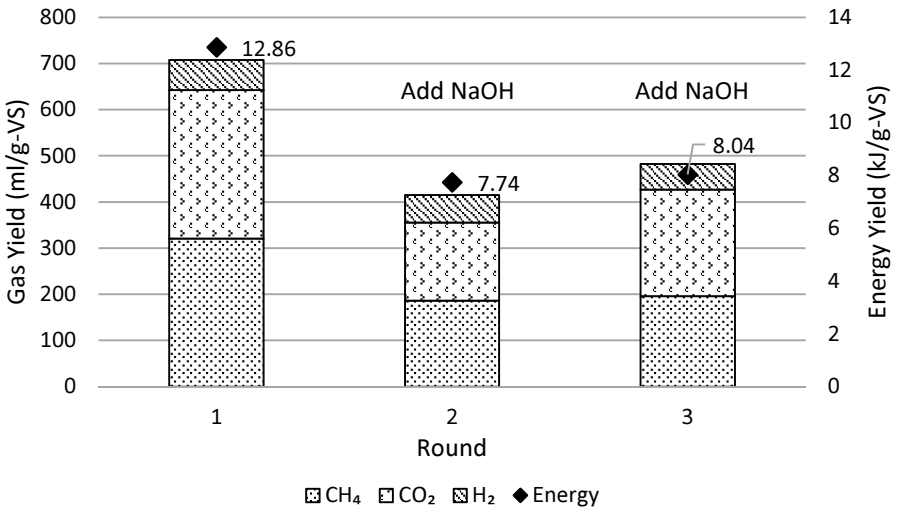

Figure 6.11 Ra-Ni Lifetime with Routine NaOH Addition, HCG of Newspaper
(30 min at 350°C, 83% moisture, 1.57 feed:Ra-Ni catalyst ratio, Rounds 2-3 4.59 feed:NaOH catalyst ratio)

With the addition of NaOH on round 2, the drop in energy yield (40%) was only slightly less than the drop observed with no NaOH addition (47%). Nevertheless, NaOH still acted to reduce the amount of carbon dioxide present in the gas phase. Thus, NaOH addition may improve second-round gasification yields, but its energy benefit is minor. The most significant difference, however, was found in round 3 with NaOH addition. Further addition of NaOH in round 3 maintained the gasification efficiency and energy yield achieved in the second round. Specifically, round 3 methane yield was held constant. Since NaOH on its own only acts to produce hydrogen and carbon dioxide gas, the methane must have been produced by Ra-Ni. Thus, the addition of NaOH extended Ra-Ni activity. The mechanism by which this occurs is hypothesized to be through the production of additional hydrogen gas that replenishes Ra-Ni's supply of adsorbed hydrogen. Park et al. (1986) attributed Ra-Ni efficiency loses to hydrogen liberation, and yielded 95 – 100% activity recovery by ex-situ 17% NaOH regenerative treatment. HCG with Ra-Ni and routine NaOH co-catalyst addition has shown its potential to maintain consistently high methane and energy yields over two rounds. More subsequent rounds or continuous operation are required to determine how long the lifetime is extended. Nevertheless, assuming $0.03/kg-NaOH (European Commission, 2001), only 397 total runs at the current energy yields would be required to economically break even—a 4.5x improvement over no NaOH addition.

To minimize costs further, the feed:NaOH catalyst ratio should be optimized. Therefore, experiments were performed to determine the effects of different co-catalytic NaOH loadings. The results are shown in Figure 6.12, with the corresponding feed:NaOH ratio. Ra-Ni was added at a 2.8 feed:catalyst ratio. Higher NaOH co-catalyst loadings increased hydrogen production and reduced carbon dioxide presence with an overall increase in energy yield. As expected, hydrogen yield increased with higher NaOH loadings. Methane yields were more than 2x greater with the application of NaOH co-catalyst, although there was no difference between the two NaOH loadings. Thus, there appears to be an optimal feed:NaOH ratio above 1.83 in which methane yield is maximized while minimizing the amount of NaOH used.

(Muangrat et al., 2010b) observed similar product distributions in the HCG of glucose with Ni/Al_2O_3 and NaOH co-catalyst at 330°C in a hydrogen peroxide medium. (Onwudili and Williams, 2013) also observed similar results in the supercritical HCG of glucose with Ru/Al_2O_3 and NaOH co-catalyst. Compared to using Ru/Al_2O_3 alone, hydrogen production nearly doubled, carbon dioxide production decreased from 17-18 mol/kg-glucose to nearly 0, while methane yield remained equivalent. Compared to NaOH alone, methane yield was roughly 4x greater in exchange for a 25% reduction in hydrogen yield, while carbon dioxide yield was also low (<1 mol/kg-glucose). It was also shown that hydrogen yield increased and carbon dioxide yield decreased, while methane yield was unaffected by increasing co-catalytic NaOH loading.

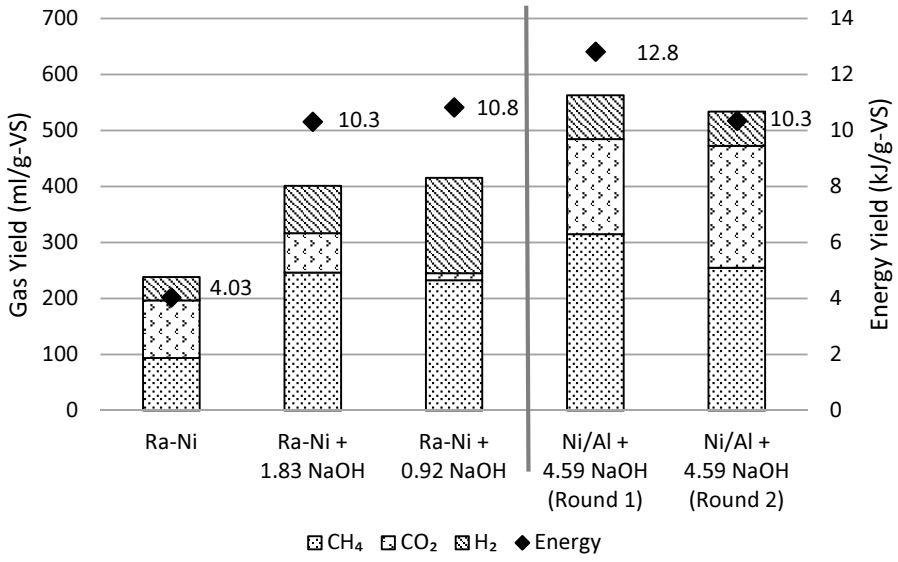

Figure 6.12 HCG with Raney Nickel and NaOH Co-Catalyst
(30 min at 350°C, 83 – 86% moisture, 2.8 feed:Ra-Ni catalyst ratio, feed:NaOH catalyst ratio in axis label)

Due to the safety hazards of Ra-Ni's pyrophoric attribute, HCG with Ra-Ni would have some limits on appropriate applications. However, if Ra-Ni could be synthesized on site from its more stable precursors (Ni/Al alloy powder and NaOH) when needed and in a suitable environment (i.e. inside the HCG reactor), it would eliminate the possibility of accidental, spontaneous Ra-Ni fires or explosions. This method also has the potential to take advantage of the hydrogen gas typically produced from Ra-Ni synthesis, as well as the benefits from using NaOH as a co-catalyst to Ra-Ni. The two rightmost bars in Figure 6.12 show the results of two sequential rounds of HCG with in-situ Ra-Ni synthesis. Ni/Al alloy powder was added to produce a 2.8 feed:Ra-Ni ratio, assuming all Ni would be converted into Ra-Ni. The production of methane in round one shows the successful in-situ development of Ra-Ni. If the Ni/Al alloy had not transformed into Ra-Ni, methane would not be present in the product gas. Compared to HCG with ex-situ-synthesized Ra-Ni, HCG with in-situ Ra-Ni synthesis increased methane production from 156 to 315 ml/g-VS, and it was even higher than the yields attained with NaOH co-catalyst. This may be attributed to the freshness of the Ra-Ni catalyst and the evolution of supplementary hydrogen gas from the Ra-Ni synthesis reaction. In the second round, all materials and liquids were kept in the reactor, and newspaper and NaOH were added at the same loading rate. Methane production and total energy yield dropped by 19% and 20%, respectively. Nevertheless, methane yield was twice as high as first-round HCG with ex-situ Ra-Ni, and was comparable to first-round HCG with ex-situ Ra-Ni and NaOH co-catalyst.

It is unknown whether the presence of sodium aluminate and aluminum hydroxide had an effect, but it can be said that their presence was not detrimental to Ra-Ni activity. There had previously been concern that the aluminum byproduct of Ra-Ni synthesis could cake the Ra-Ni catalyst. Soluble sodium aluminate forms at high NaOH concentrations whereas aluminum hydroxide, which precipitates as $Al(OH)_3$ bayerite, forms at low NaOH concentrations, as Equations (6.5) and (6.6) help illustrate. Bayerite deposited onto the surface of Ra-Ni would decrease the amount of active surface area, and therefore was expected to possibly lower the catalyst's activity. Ertl et al. (2008) notes that 20 – 40% excess weight of NaOH is required to avoid aluminum hydroxide formation. However, Nishimura et al. (1991) and Taira and Kuroda (1970) showed that bayerite promoted the formation of more active Ra-Ni. Since we did not observe Ra-Ni activity loss, but rather the opposite, with in-situ Ra-Ni synthesis, it is possible that the higher methane yield is due to the concurrent formation of bayerite.

$$2Al + 6H_2O \rightarrow crystalline\ 2Al(OH)_3 + 3H_2 \quad (6.5)$$

$$NaAlO_2 + 2H_2O \leftrightarrows Al(OH)_{3,amophous} + NaOH \rightarrow Al(OH)_{3,crystal} + NaOH \quad (6.6)$$

In-situ Ra-Ni synthesis with routine NaOH co-catalyst addition is an even more promising amendment to current HCG processing with Ra-Ni. This new processing method benefits from consistently higher gas yields, lowers the cost due to the (approximately 4x) cheaper price of Ni/Al alloy powder compared to Ra-Ni, and spares the need to store hazardously pyrophoric Ra-Ni. Assuming the Ni/Al alloy powder costs $5/kg, and that the process achieves steady-state energy yield equivalent to that achieved in HCG with ex-situ-synthesied Ra-Ni and routine NaOH addition, only 90 runs are need for economic breakeven—an additional 4.4x improvement, and an overall 20x improvement over traditional approaches.

6.2.3 NaOH Requirements for Ra-Ni Synthesis

As discussed in Section 3.2.1, there is an optimal leaching of Al below 100% which maximizes Ra-Ni activity. Nishimura et al. (1991) had found that 80 – 90% Al leaching of $NiAl_3$ and Co_2Al_9 yielded the highest activity for their respective catalyst state. HCG experiments were conducted with Ra-Ni that had been synthesized ex-situ with different molar concentrations of NaOH, yielding varying levels of aluminum leaching. The results can be used to determine the optimal NaOH loading for the first-round of in-situ Ra-Ni synthesis in order to produce the most effective Ra-Ni catalyst.

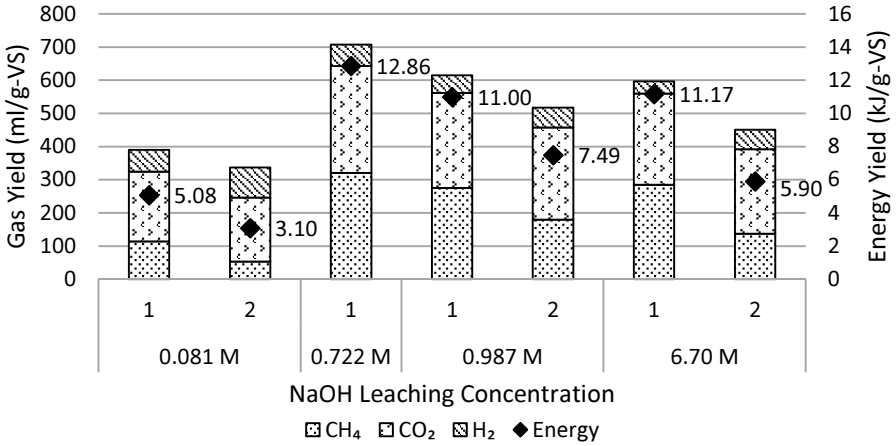

Figure 6.13 Variations in Ra-Ni Catalytic Activity as a Function of Leaching
(30 min at 350°C, 84–86% moisture, 1.57 feed:catalyst ratio)

Ra-Ni that had been leached in 0.722M NaOH yielded the highest activity. At higher NaOH concentrations, there were minor losses in overall methane yield. However, underleaching was more detrimental than overleaching. Although there is potentially a NaOH concentration between 0.081M and 0.722M that maximizes Ra-Ni activity, it is recommended to add excess NaOH to avoid underleaching.

6.2.4 Comparison of HCG to Anaerobic Digestion

HCG was proposed as a novel alternative to anaerobic digestion due to its significantly quicker reaction times and reportedly higher energy yields. Figure 6.14 shows the range of HCG yields achieved in this study overlaid with literature values for energy yields from the anaerobic digestion of newspaper. By round 5, the energy yield from conventional HCG with Ra-Ni was equivalent to AD with a 5 – 10 day HRT. However, with routine NaOH addition, HCG can potentially achieve consistent yields 2.1 – 2.8x greater in 30 minutes than AD achieves in 30 – 60 days. HCG recovered 40% of the newspaper's energetic content while conventional AD could only achieve up to 18%, which corresponds to 21% of AD theoretical maximum methane yield.

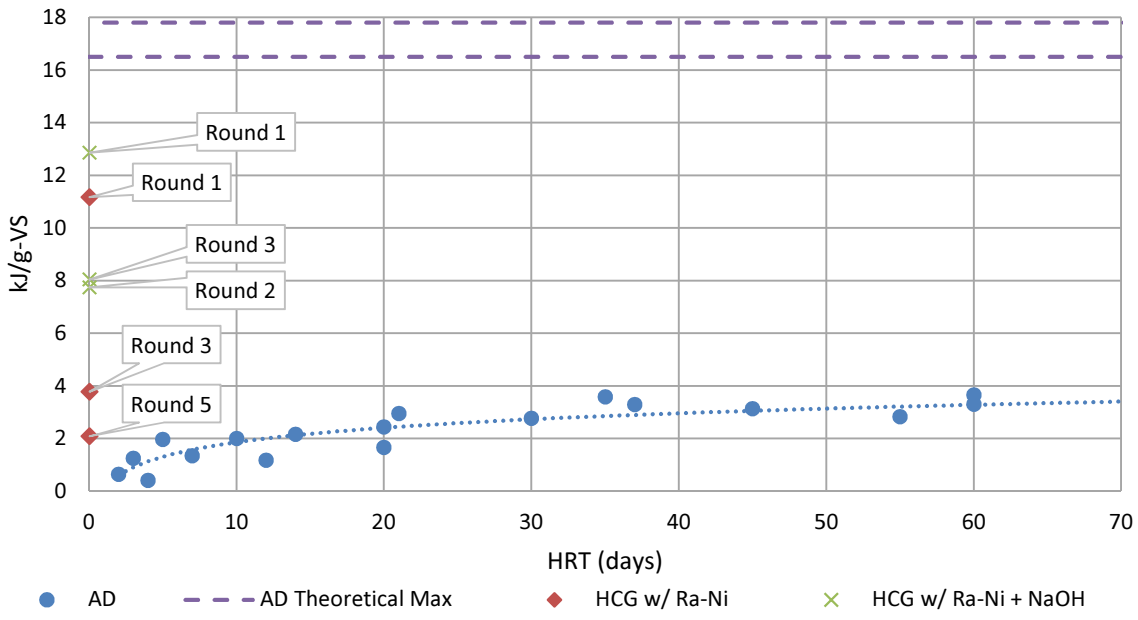

Figure 6.14 Energy Yield Comparison between HCG and AD Processing of Newspaper
AD data adapted from Clarkson and Xiao (2000), Owens and Chynoweth (2011), Tong et al. (1990), Xiao and Clarkson (1997), and Yuan et al. (2012)

Although HCG has higher conversion efficiencies than anaerobic digestion at significantly shorter retention times, HCG requires much higher temperatures and the addition of catalysts. To determine whether HCG is a net energy-producer, the operating energy of heating and embedded energy of catalyst production must be taken into account. Table 6.4 summarizes the parameters used to calculate the net energy yielded from the HCG of newspaper.

A long-term consistent energy yield of 7.89 kJ/g-VS (average of the second and third round of HCG with Ra-Ni and Routine NaOH Addition, Figure 6.11) was assumed while using the feed:catalyst ratios from the in-situ synthesis of Ra-Ni experiments. The reactor volume was specified to be 1,000 L; at this magnitude, throughput is maximized while minimizing the energy needed to initially heat the liquid medium. Given a reactor a volume of 1,000 L, the maximum processing capacity is well below what a processing facility can expect to receive—e.g. 140 to 1,200 tons/day, based upon paper recovery facilities (Maryland Environmental Service, n.d.; West Virginia Solid Waste Management Board, 2013). The reactor was also assumed to operate for only half a day, as how some gasification systems are operated. However, 24-hr operation would be the most beneficial by eliminating heat expenditure from reheating the reactor each day and heat loss at the end of daily use. Figure 6.15 shows the heat flow through the vertical cross-section of the modelled cylindrical HCG reactor.

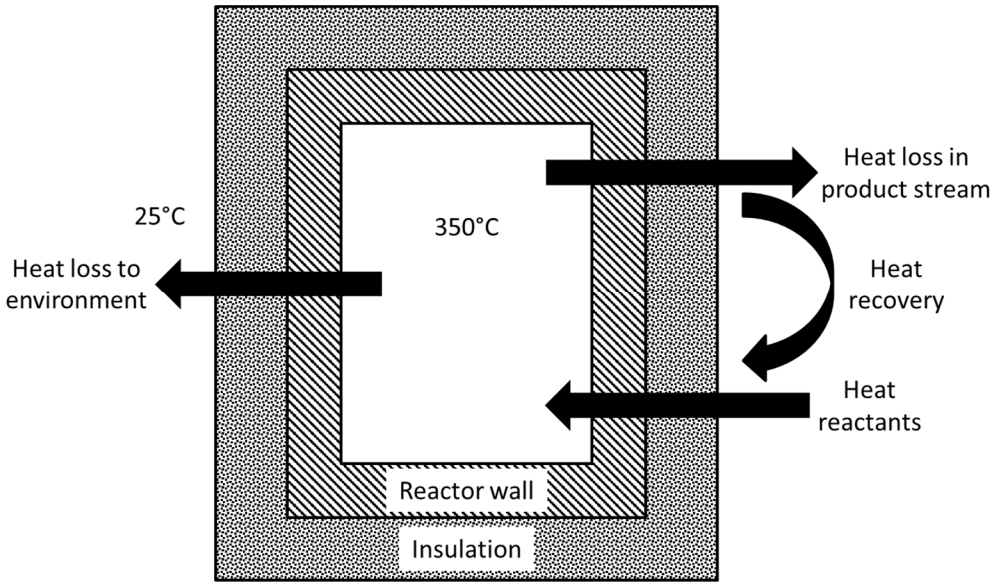

Figure 6.15 HCG Reactor Heat Flow Diagram

Table 6.4 HCG Net Energy Calculation Parameters

Heating	**Unit**	**Value**	**References**
Specific heat of paper	kJ/kg/K	1.336	
Enthalpy of sat. liq. water at 25°C	kJ/kg	104.89	
Enthalpy of sat. liq. water at 350°C	kJ/kg	1,670.60	
Energy to heat paper from 25°C to 350°C	kJ/g	0.43	
Energy to heat water from 25C to 350°C	kJ/g	1.57	
Reactor Setup and Catalyst Usage			
Reactor moisture	%wt	0.82	(This Study)
Newspaper moisture content	%wt	0.08	(This Study)
Feed:catalyst ratio	g-TS-paper/g-Ra_Ni	1.57	(This Study)
Feed:catalyst ratio	g-TS-paper/g-NaOH	4.59	(This Study)
HCG conversion	kJ/g-TS-paper	7.85	(This Study)
Ra-Ni Lifetime	Rounds	100	(Shimizu and Suniita, 1975)
	g-TS-paper/g-Ra_Ni	157.10	
Primary production of Ni (pyrometallurgy)	kJ/g-Ni	114	(Norgate and Rashkin, 2000; Rankin, 2012)
Primary production of Al	kJ/g-Al	180	(Lavery et al., 2013)
Metal casting and crushing	kJ/g-NiAl	2.88	(Lavery et al., 2013)
50/50 NiAl alloy embedded energy	kJ/g-NiAl	137.67	Calculated
50/50 NiAl alloy conversion to Raney-Ni	g-Ra_Ni/g-NiAl	0.69	Assume 1 mol Ra_Ni / 1 mol NiAl
NaOH Fabrication (chloralkali process)	kJ/g-NaOH	9.71	(European Commission, 2001)
Operation Assumptions			
Reactor volume	L	1,000	
Reactor radius	m	0.35	
Reactor working volume	L	800	
HRT	days	0.02	
Working hours	hrs	12	
Heating Efficiency	%	0.80	
Heat Recovery	%	0.70	
Reactor wall thickness	m	0.15	
Reactor wall (stainless steel AISI 302) thermal conductivity	W/m/K	20.34	(Incropera et al., 2007)
Insulation thickness	m	0.5	
Insulation (alumina-silica fiber) thermal conductivity	W/m/K	0.738	(Incropera et al., 2007)
Heat Loss to Environment	kJ/hr	22,642	Calculated
Calculations			
Max processing capacity	dry tons/day	3.39	

Figure 6.16 provides a sensitivity analysis, showing the net energy yield achieved for processing 200 tons of dry newspaper at varying heat recoveries and heating efficiencies. HCG can yield a positive net energy balance even with no heat recovery at 80% heating efficiency, and above 10% heating efficiency at 70% heat recovery.

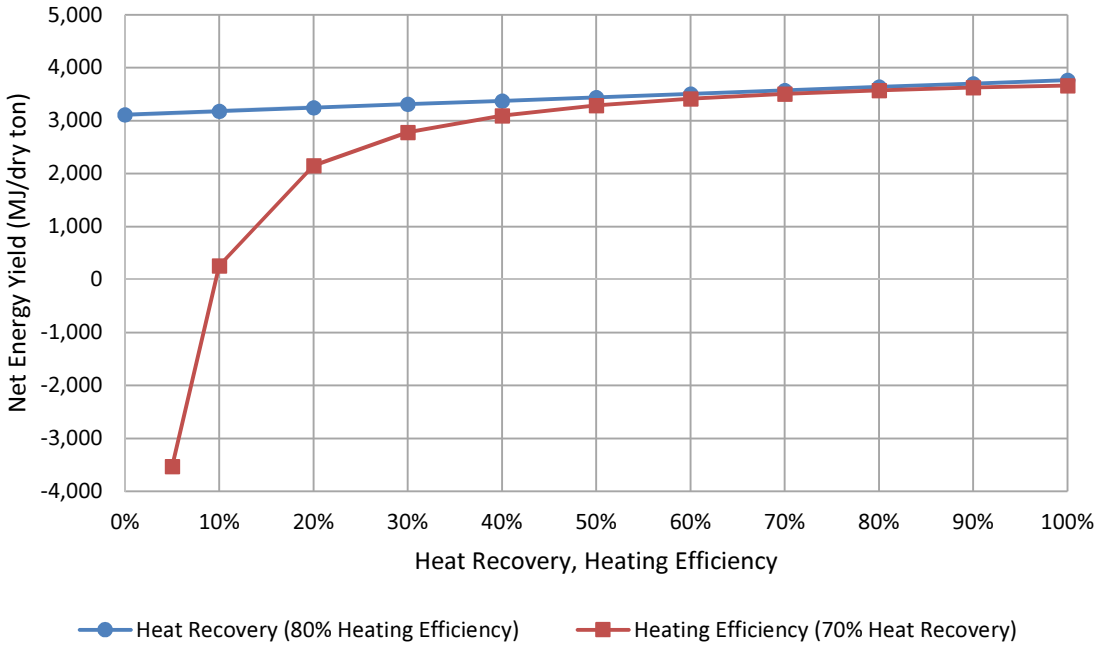

Figure 6.16 Effect of Heat Recovery and Heating Efficiency on HCG Net Energy Yield
(In order to process 200 tons of dry newspaper)

A model for the net energy yield from the operation of an anaerobic digestion process was then established, with parameters relating to those chosen for HCG—i.e. reactor size, working volume, and heating efficiency (Table 6.5). AD conversion value and its corresponding HRT were selected based upon maximizing energy yields while minimizing retention time. The digester would be operational 24 hours/day, as is typical for AD systems. Chynoweth et al. (1993) observed maximum conversion rates using a feed:inoculum ratio of 2 g-VS_{feed}/g-VS_{sludge} when treating a variety of biomass and waste feedstocks.

Table 6.5 AD Net Energy Calculation Parameters

Heating	**Unit**	**Value**	**References**
Specific heat of paper	kJ/kg/K	1.336	
Enthalpy of sat. liq. water at 25°C	kJ/kg	104.89	
Enthalpy of sat. liq. water at 35°C	kJ/kg	146.68	
Energy to heat paper from 25°C to 35°C	kJ/g	0.01336	
Energy to heat water from 25°C to 35°C	kJ/g	0.04179	
Reactor Setup			
Sludge moisture content	%wt	0.98	(R. Zhang et al., 2005)
Sludge VS content	%	0.01	(R. Zhang et al., 2005)
Paper VS content	%	0.91	(This Study)
Density of paper	dry g/L	610	
Paper moisture content	%wt	0.083	(This Study)
AD Conversion	kJ/g-VS	2.16	(Xiao and Clarkson, 1997)
	kJ/g-TS	2.15	
Operating Assumptions			
Reactor volume	L	1000	
Reactor working volume	L	800	
Paper loading	g-VS_paper/g-VS_sludge	2	(Chynoweth et al., 1993)
HRT	days	14	(Xiao and Clarkson, 1997)
Working hours	hr	24	
Heating Efficiency	%	0.70	
Heat Recovery	%	0	
Heat Loss to Environment	kJ/hr/L	0.034	(Smith et al., 1979)
Calculations			
Max processing capacity	dry g/day	1,206	
	dry tons/day	0.00133	

Equation (6.7) presents the terms used to calculate net energy yield for HCG and AD. For the AD systems, the energy costs of Ra-Ni and NaOH production were zero since no catalysts are used.

$$Net\ Energy\ Yield = (Energy\ Production) - Heating - (Ra\text{-}Ni\ Production) - (NaOH\ Production) \quad (6.7)$$

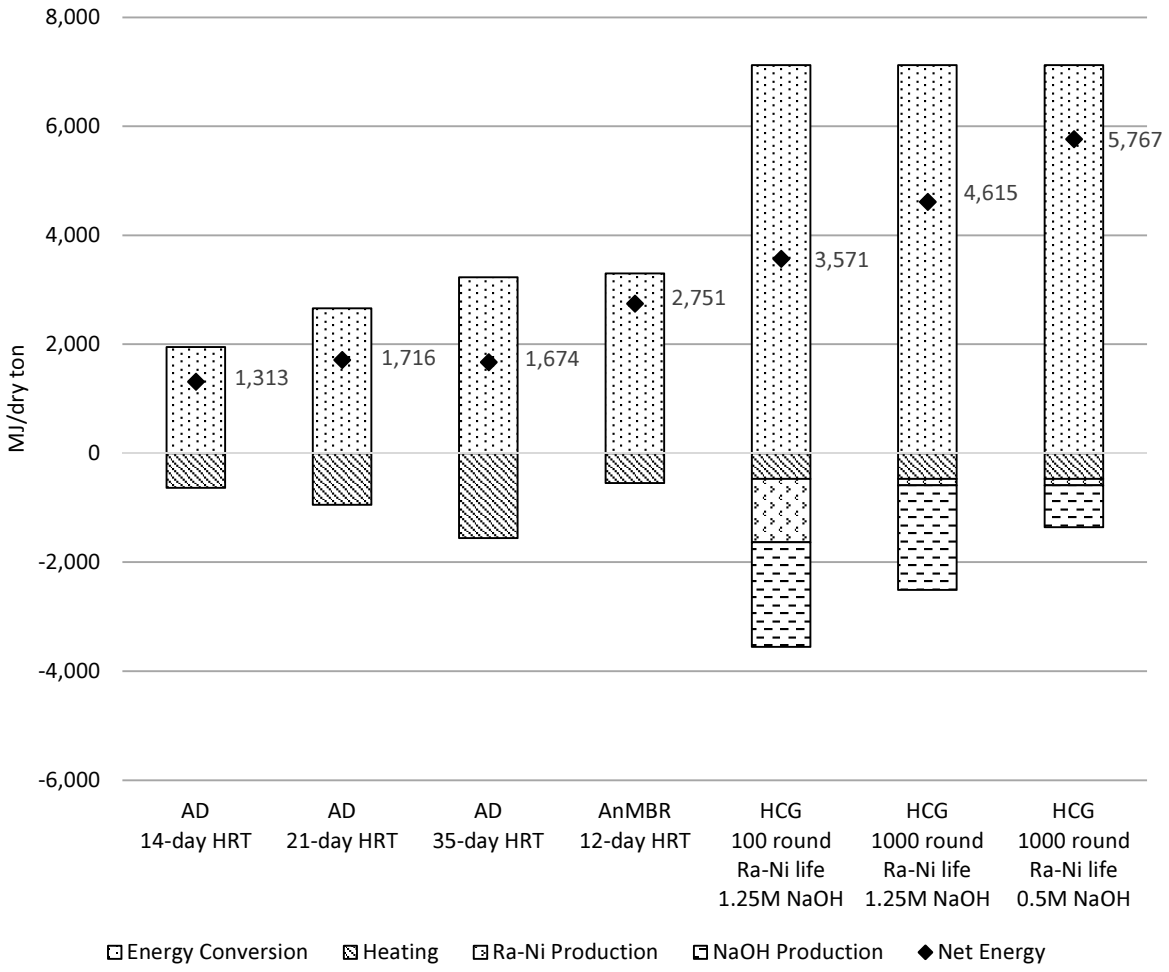

Figure 6.17 HCG and AD Net Energy Balance (200 tons dry newspaper)

Figure 6.17 shows the results from applying the HCG and AD models for net operating energy with different assumptions. The values on the side of each bar indicate the total net energy yields. HCG heating efficiency was assumed to be 80% while heat recovery was assumed to be 70%, which may be achievable with such a system. AD heating efficiency was assumed to be 80% with no heat recovery. AD has smaller energy inputs due to not needing catalysts, and can achieve a positive energy balance with less input material than HCG systems. However, after processing 0.76 dry tons, HCG will net more energy than 14-day HRT AD. On a net energy basis, HCG is more competitive than conventional anaerobic digestion and AnMBRs (assuming maximum achievable digestion at 1/5 the HRT of conventional AD). Since catalyst usage is the largest energy demand for HCG, it is therefore imperative that extending catalyst lifetime should be the focus of future study. Figure 6.17 also shows that the current amount of

NaOH used for in-situ Ra-Ni regeneration creates the greatest energy burden on HCG. This reveals the importance of finding the minimal NaOH loading needed for Ra-Ni regeneration.

Nevertheless, HCG is advantageous in terms of the high rate of conversion. HCG benefits from being able to process material on the timescale of 30 – 60 minutes while AD may typically take 20 – 40 days. Thus, although the energy analysis assumed equivalent reactors sizes, HCG reactors are 2 – 4 magnitudes smaller and they allow for conversion of more material that might otherwise go unused. For equivalently sized 1,000 L reactors, the modeled AD system requires 150,447 days of continuous operation while the HCG system requires only 30 days of half-day operation to process 200 dry tons of newspaper. An HCG system can therefore generate more energy on a daily basis than conventional AD and AnMBR systems treating newspaper.

However, HCG's higher heating requirements may lead to AD being more energetically favorable when processing organics with high moisture contents. Energy analysis with newspaper feedstock, taking into account operational heating and catalyst embedded energy costs, has shown that HCG can be more favorable than AD for moisture contents less than 49%, assuming 70% HCG heat recovery, while AD of newspaper is net energy negative at moisture contents greater than 68%. If time-dependent heat and energy loses are included, HCG can be favorable at even higher moisture contents. For newspaper's original moisture content of 8%, net energy production can be roughly 2x greater with HCG than AD. Nevertheless, even if HCG has a lower net energy yield (e.g. 2x less), it can be more than made up for by the roughly 670x higher processing speed.

CHAPTER 7

SUMMARY AND CONCLUSIONS

This study investigated the performance of a two-phase anaerobic membrane bioreactor (AnMBR) system treating municipal wastewater primary sludge, and the effects of applying routine bioaugmentation to the system's AP reactor. The start-up time of the AnMBR system fell within the average of other reported AnMBR systems; the AP took 6 weeks while the MP took 8 – 9 weeks, although high microbial activity was already achieved by week 6. At steady-state, the non-bioaugmented AnMBR system achieved high TCOD removal of > 99% and high methane yields of 98%. These results are superior to those reported of conventional digesters (60% – 70%), sludge blankets (up to 90%), and even other AnMBR systems (around 95%). Current results on bioaugmentation support the notion that bioaugmentation will not improve, and can be potentially detrimental, in a system that has already achieved a high level of performance in terms of COD solubilization, COD reduction, and methane production. Bioaugmentation resulted in higher SCOD and VFA concentrations in the AP, but increased MP sulfide production and a caused a statistically minor reduction in methane yield. Nevertheless, bioaugmentation is still expected to provide advantages when an AD system is under stress. Higher loading rates and shorter retention times were tested in an attempt to induce stress, but the system was still able to maintain high levels of performance.

This study also evaluated the performance of hydrothermal catalytic gasification (HCG) on a lignocellulosic feedstock and sought improvements extend to catalyst lifetime. Initial results showed effective HCG of newspaper with Raney nickel (Ra-Ni) catalyst at 350°C for 30 min. However, catalyst lifetime was too short for economic feasibility. Preliminary HCG experiments with Ra-Ni and routine addition of NaOH showed significant improvements in prolonging catalyst lifetime. Based upon these results, an analysis of front-end energy costs—which includes the catalysts' embedded energy and reactor heating requirements—showed that HCG with Ra-Ni can net generate up to 60% more energy on a mass basis than anaerobic digestion, and within the timeframe of minutes rather than days. HCG with in-situ Ra-Ni synthesis and routine NaOH addition can be economically and energetically viable given a catalyst lifetime greater than 55.8 g-newspaper/g-catalyst, and a well-designed system with

efficient heat recovery and suitable operating parameters. HCG is more competitive than conventional anaerobic digestion, and at high catalyst lifetimes, HCG can also net more energy than AnMBRs.

CHAPTER 8

RECOMMENDATIONS AND FUTURE WORK

Benefits from bioaugmentation are expected to be observed in an AnMBR system under greater stress, where the anaerobes are significantly unable to process incoming organics as fast as they are removed. The following points outline methods by which this can be achieved.

- The system can be stressed by applying a lower HRT in the acid-phase reactor, and a lower HRT and/or SRT in the methane-phase reactor. Membrane fouling problems associated with HRT reduction, as experienced in this study, can be overcome by changing the MP reactor design. First, the mechanical mixer should be removed from the MP reactor in order to allow enough safe space for the sediment filters to be replaced with large bundles of loosely-bound or unbounded hollow-fiber membranes. A gas pump will recirculate MP headspace gas and provide sparging from the bottom of the MP reactor, thereby providing mixing and membrane scouring. A programmable pump should also be set to regularly provide small backwashing pulses of effluent several times per hour.

- Alternatively, the AnMBR system can be stressed by turning off the heat adjustment and operating the AP and MP reactors at room temperature. Lower temperatures are expected to induce slower microbial metabolism and growth. Past experience has shown an immediate reduction in biogas production when the heating had been left off overnight.

The dry bioaugmentation culture could also be developed further for enhanced acetogenesis. Furthermore, the AP pH should be regulated to ensure uninhibited anaerobic digestion so that less substrate can be used by sulfate reducers. To accomplish this, higher bioaugmentation loadings of anaerobic sludge can be leveraged to increase the AP pH to more optimal conditions (~pH 6) using the recycled, pH-controlled methanogenic sludge.

As for HCG, economic feasibility still poses some question since a strongly influential parameter—catalyst lifetime—remains unknown. The following bullet points outline the logical next steps for future work in this area:

- The next task is to perform further consecutive rounds, or continuous operation, of HCG with Ra-Ni and routine NaOH addition in order to measure the extent to which Ra-Ni lifetime can be prolonged. Meanwhile, Ra-Ni fouling and poisoning should be analyzed, prospectively using environmental scanning electron microscopy (ESEM) along with EDAX light-element energy-dispersive spectroscopy (EDS).

- Chemical analyses of the liquid-phase and solid-phase analysis should be performed to determine effluent quality and overall carbon distribution, which relate to the production rate of aluminum byproducts and sodium carbonate/bicarbonate.

- Tests at different feed:Ra-Ni:NaOH:water ratios should be conducted to determine the optimum balance between net energy yield, Ra-Ni regeneration, and carbon dioxide removal. Along this line, higher feed:NaOH ratios should be tested to be able to plot the downward trend in methane and energy production as less NaOH is used. Cost and energy analyses should then be carried out on these results.

- Ra-Ni activity can be maximized by finding the optimum NaOH loading during the in-situ synthesis of Ra-Ni.

As part of future work, it was mentioned that the aqueous and solids products of HCG be analyzed and accounted for. One compound that will certainly be present is sodium aluminate. Sodium aluminate removal from wastewater present challenges since over a wide range of pH values they precipitate into gel-like, poorly filterable hydroxide. However, upon carbonating the aluminate solutions the filtration coefficient of the hydroxide precipitates is increased by a factor of 500 – 1,000 (Vasserman, 1980). These aluminum hydroxide precipitates have been considered for use as raw material for the production of high-alumina cement or as a filler for

refractory concrete (Arsenova et al., 1988). Aluminum hydroxide has also been applied as a flocculant for sludge dewatering and algae removal (Schlesinger et al., 2012).

HCG may also have potential in processing synthetic organic compounds (i.e. plastics). Catalytic gasification of plastics has been studied in unpressurized air (Ishihara et al., 1990; Sancho et al., 2008) and steam (Wu and Williams, 2009) environments, but not under hydrothermal conditions. HCG may similarly be able to process petroleum-derived plastics into methane and hydrogen gas, but can be advantageous due potentially lower production—or rather, higher destruction—of toxic dioxins and dioxin-like compounds. Dioxins—a class of halogenated organic molecules—are highly toxic persistent organic pollutants that have adverse health effects and are carcinogenic. All current major plastics disposal and energy conversion technologies—incineration, pyrolysis, combustion, gasification, etc.—produce dioxins as a byproduct. Prospectively, HCG with Ra-Ni or Ru can gasify the organics and simultaneously destroy dioxins as they are produced. Raney nickel is known to be an effective catalyst for the dehalogenation of organic halides, with the exception of some fluorine and vinyl halides (Barrero et al., 2001). For example, Wu et al. (2005) reported 20% dehydrochlorination of a chlorobenzene solution into benzene using Raney nickel with NaOH under the following conditions: 1.0 MPa H_2 pressure, 60 min, and 343 K. Ra-Ni has also been shown to perform complete dehalogenation 4-bromoaniline and 4-chloroaniline into aniline (Weidlich et al., 2010), complete debromination of 4-bromobiphenyl (Liu et al., 2010), complete dehalogenation of polyhalogenated anilines (Weidlich and Prokeš, 2011), and acts to debrominate 4-bromoacetanilide and dechlorinate 4-chloroacetanilide (De Koning, 1975). Consequently, it may be of interest to further investigate this potential HCG feedstock and use of Ra-Ni.

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APPENDIX A

ADDITIONAL ANMBR DATA

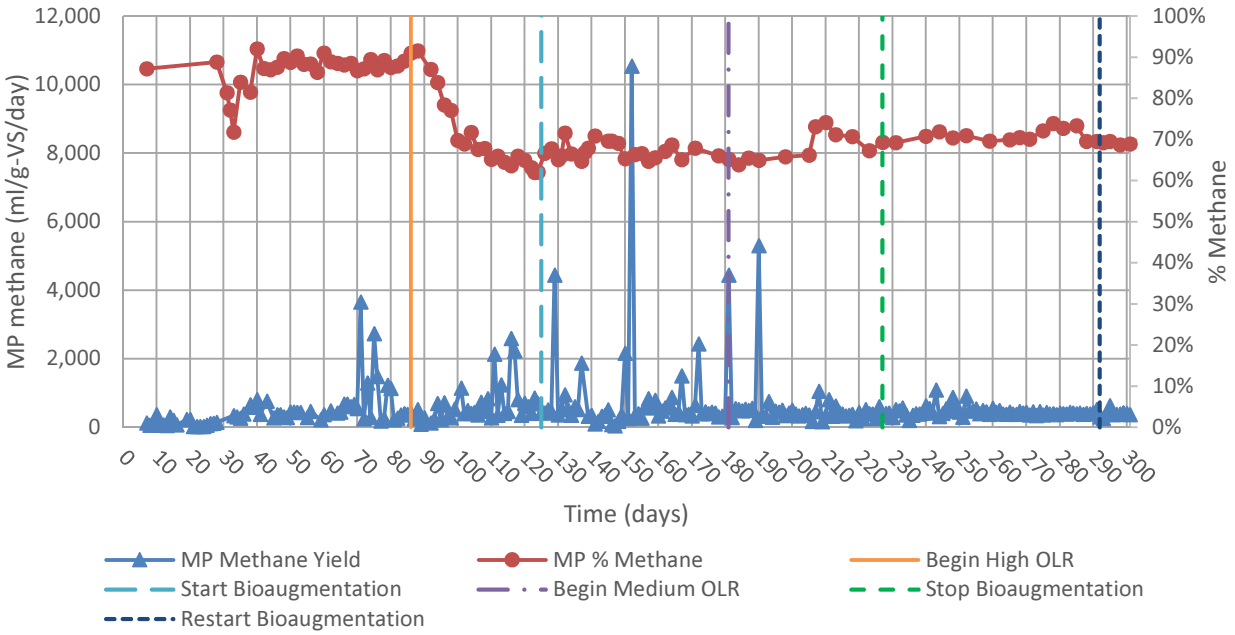

Figure A.1 Raw Methane-Phase Methane Yield

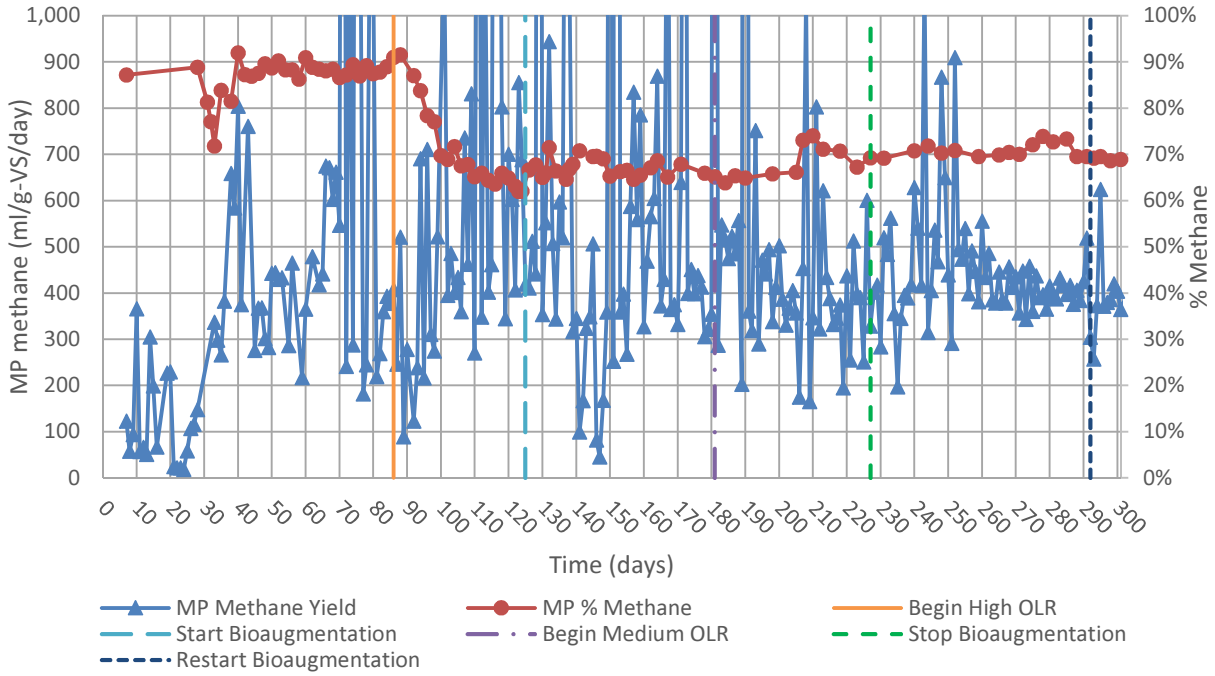

Figure A.2 Raw Methane-Phase Methane Yield (Zoomed In)

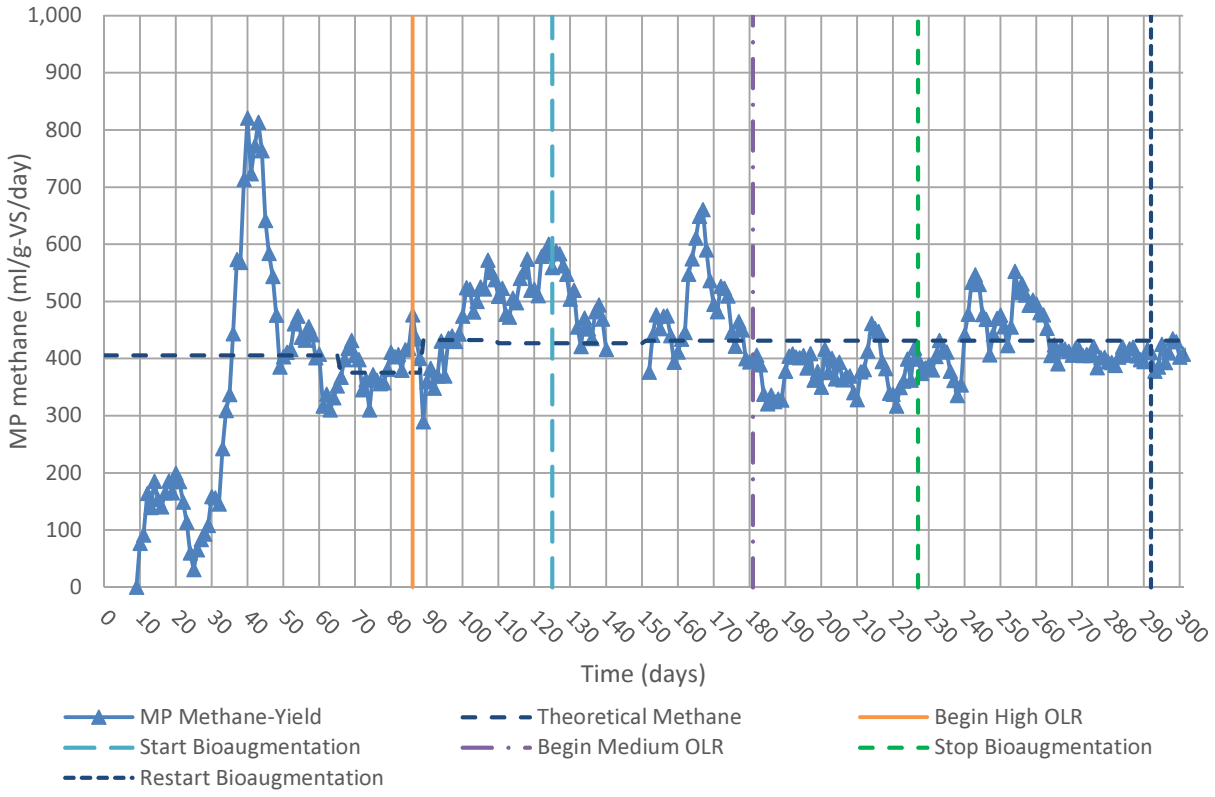

Figure A.3 Methane-Phase Methane Yield (5-Day Moving Average)

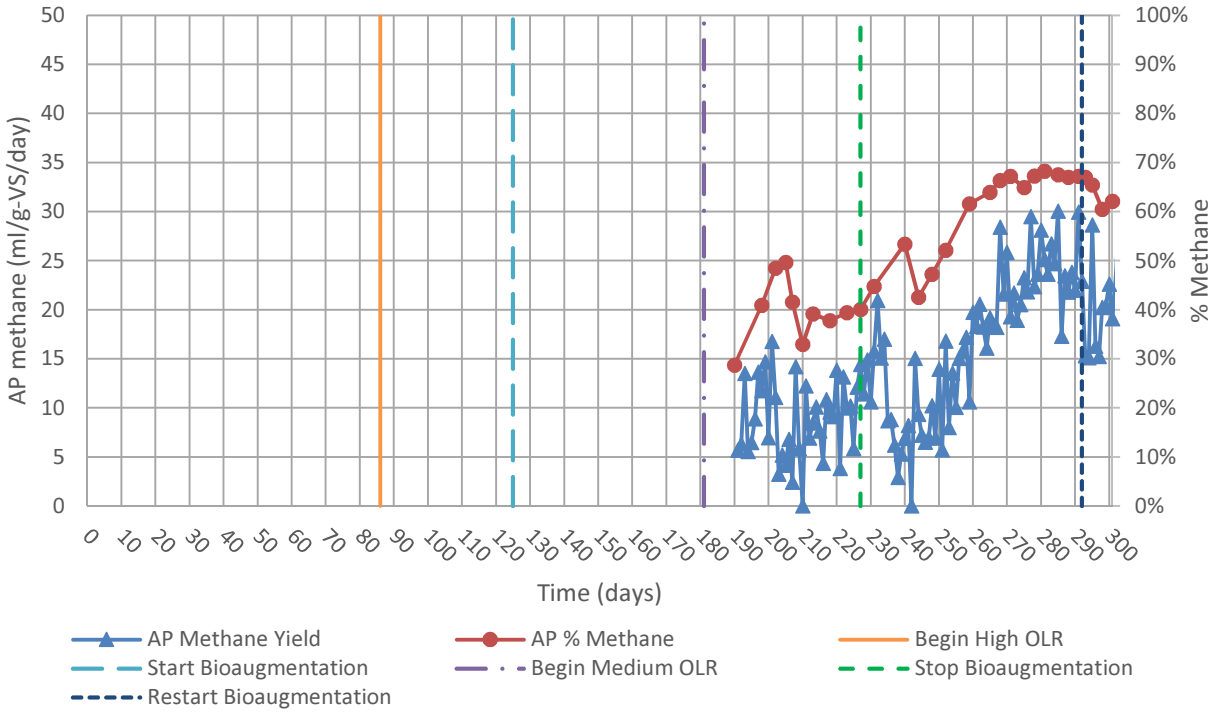

Figure A.4 Acid-Phase Methane Yield

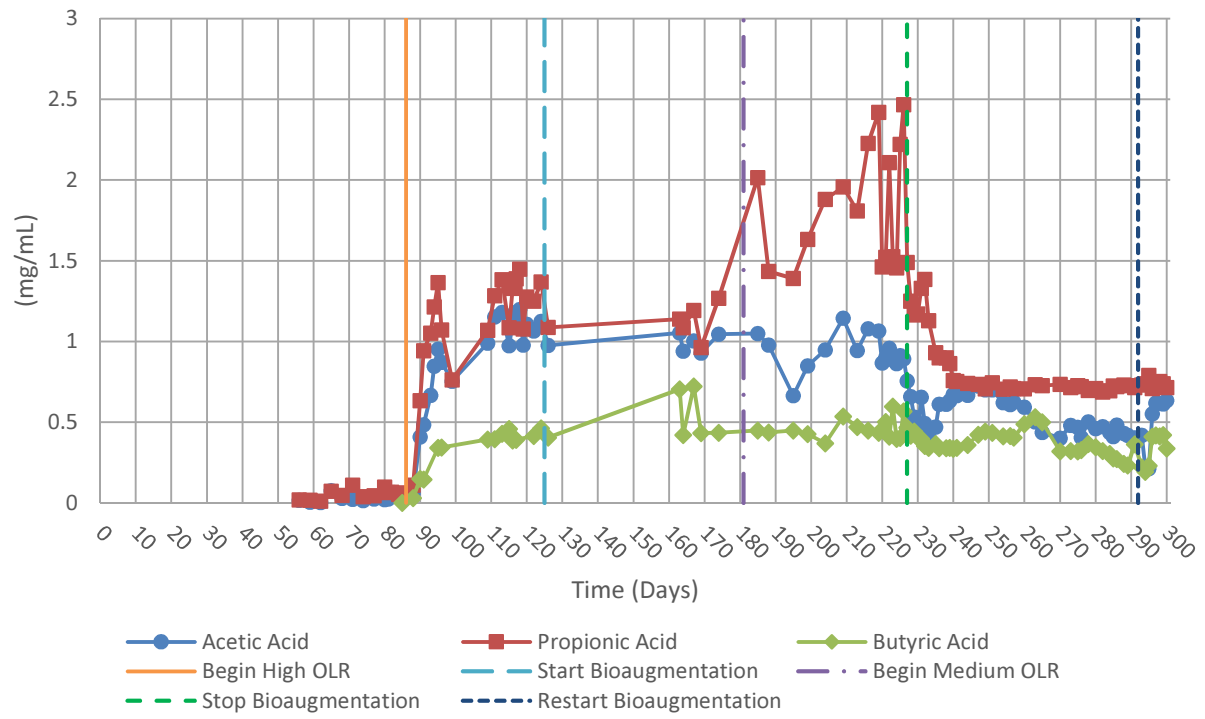

Figure A.5 Acid-Phase VFA Concentrations

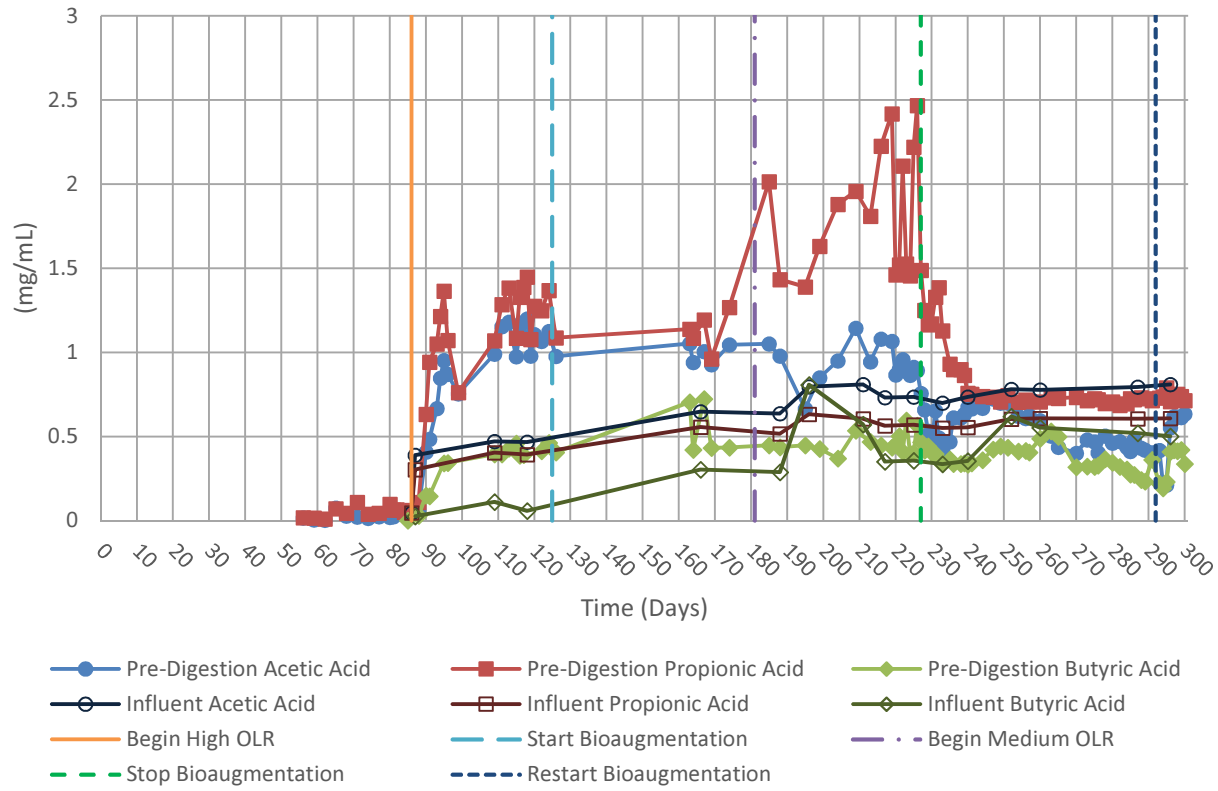

Figure A.6 Influent and Acid-Phase VFA Concentrations

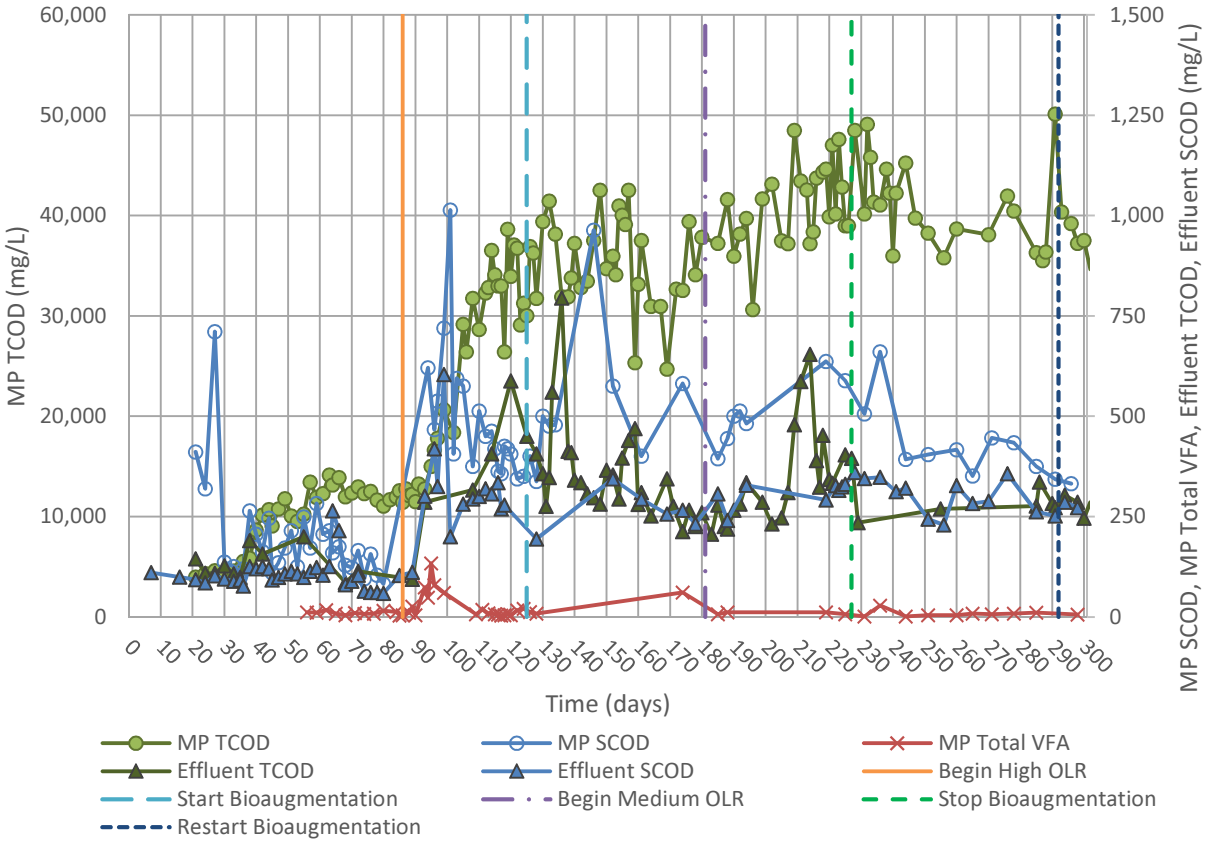

Figure A.7 Methane-Phase and Effluent Organics Concentrations

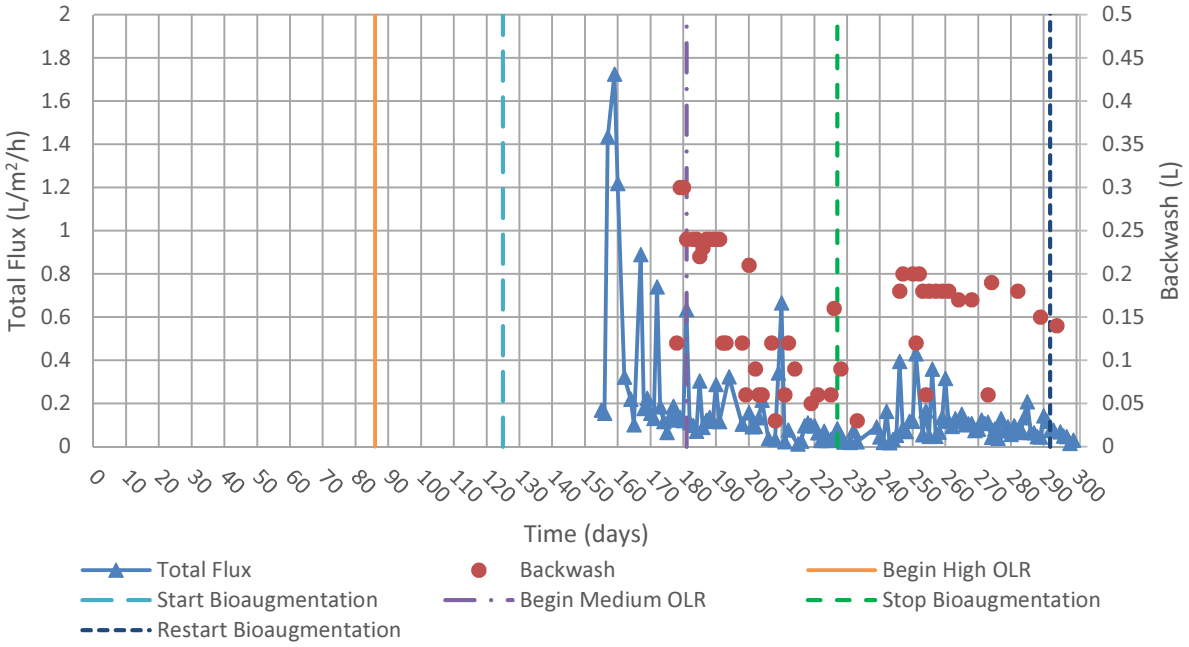

Figure A.8 Daily Total Flux through Methane-Phase Membranes

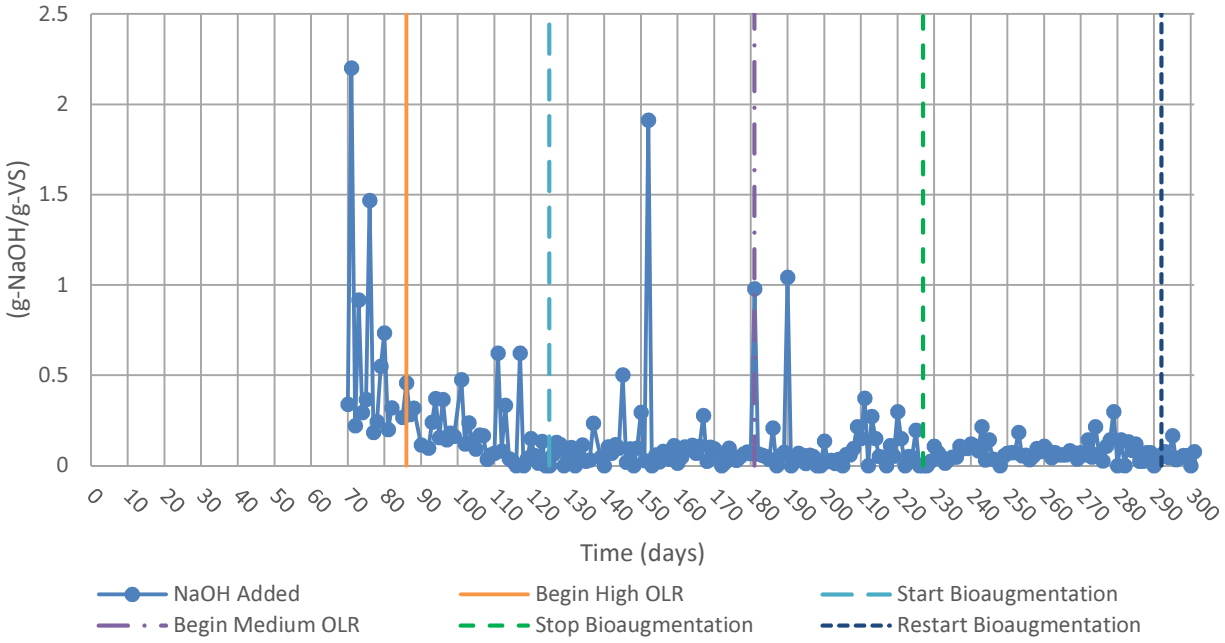

Figure A.9 NaOH Required to Maintain Methane-Phase at pH 7

APPENDIX B

ADDITIONAL HCG DATA

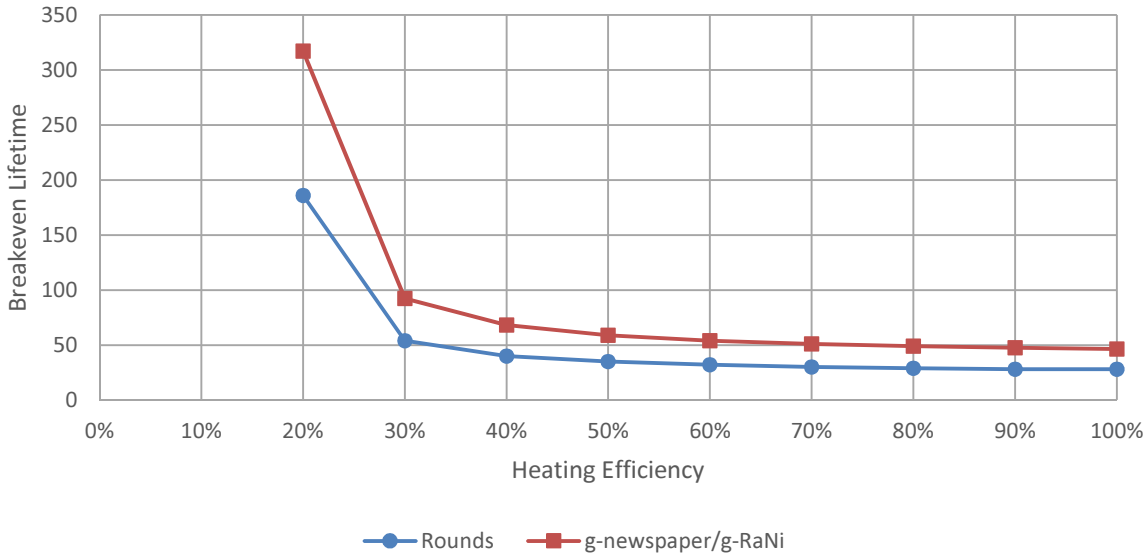

Figure B.1 Effect of Heating Efficiency on HCG Catalyst Breakeven Lifetime
(Assume 0% heat recovery)

The minimum efficiency to breakeven at a 100 rounds lifetime is 22.6%. Sensitivity analysis found that a positive energy yield can be attained for reactors and working volumes of any size. Analysis also revealed that the minimum number of continuous operating hours per day to breakeven energy is 7.44 hours—1.43 tons/day—at 30% heating efficiencies and 1.61 hours—0.31 tons/day—at 100% heating efficiencies.

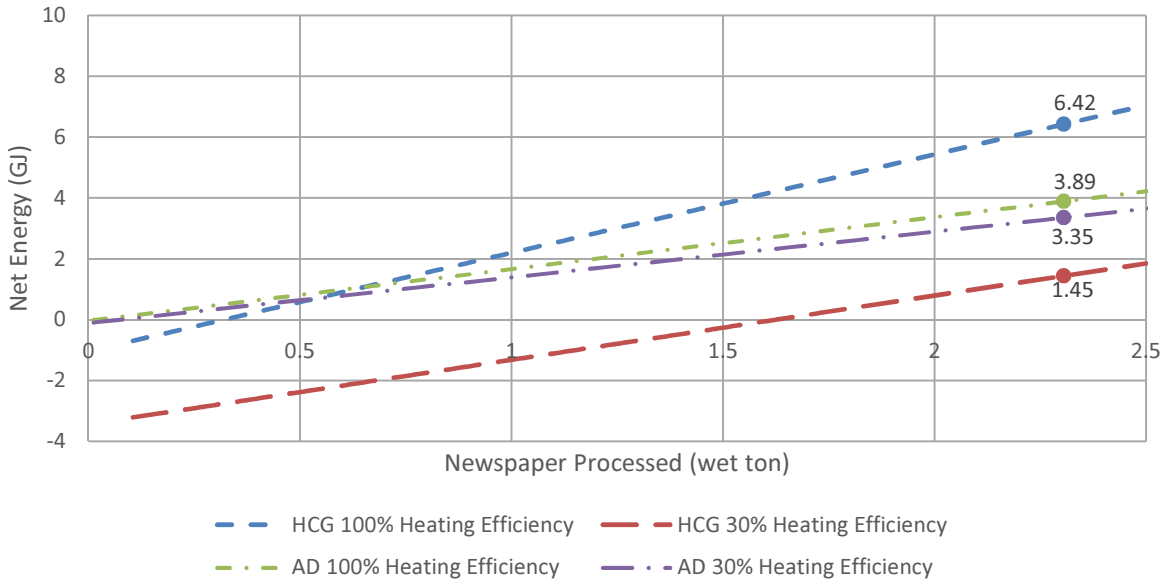

Figure B.2 Comparison of HCG and AD Net Energy Yields, with Heating Efficiencies
(Points marked at maximum amount of newspaper processed per day by modeled HCG system, 0% heat recovery)

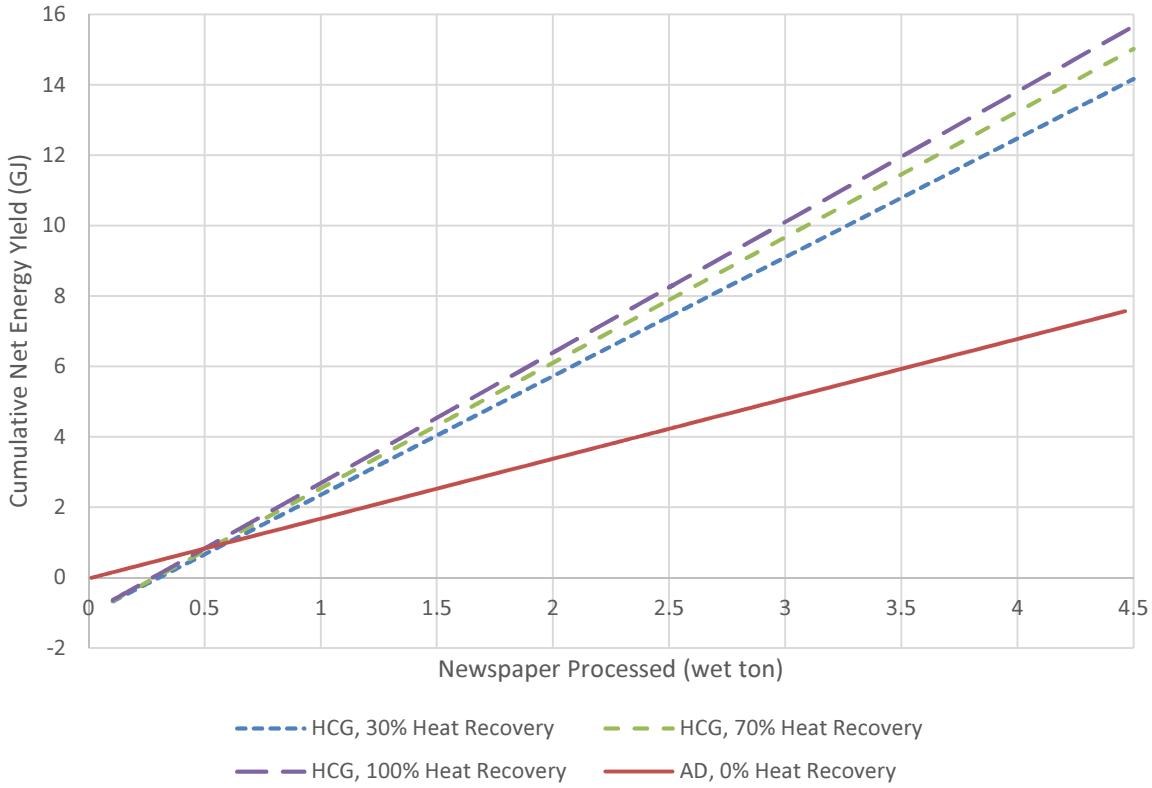

Figure B.3 HCG and AD Cumulative Net Energy Yields, with Heat Recovery

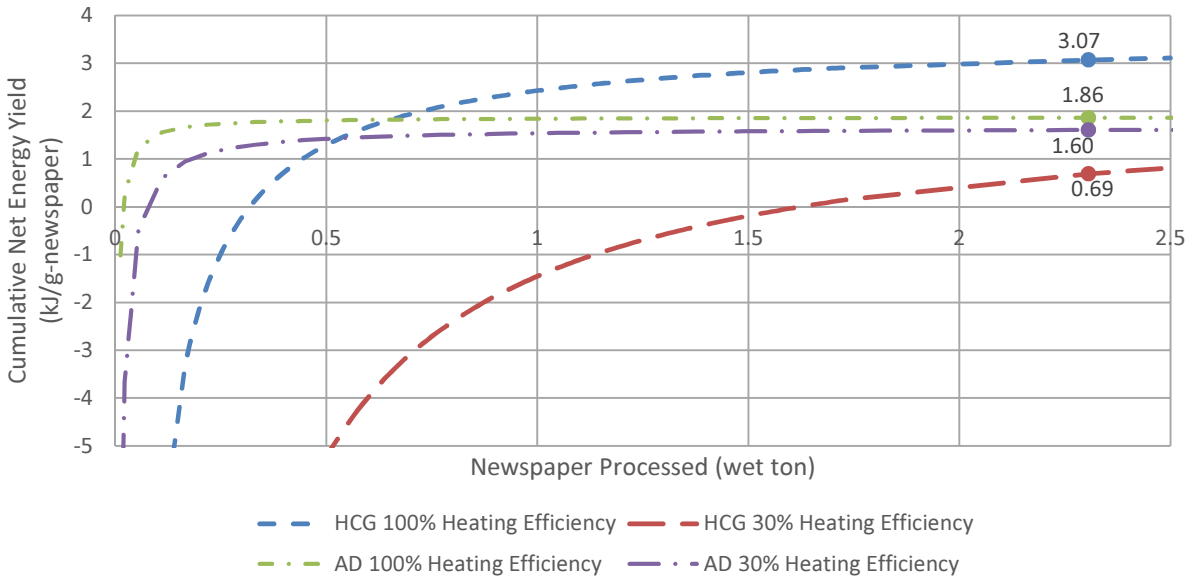

Figure B.4 HCG and AD Steady-State Energy Yields, with Heating Efficiencies
(Assume 0% heat recovery)

HCG systems are affected greater by the heating efficiency, due to their high throughput of material. HCG can achieve higher net energy yields than anaerobic digestion when the heating efficiency is above 42.9%. At heating efficiencies less than 42.9%, AD has higher performance.

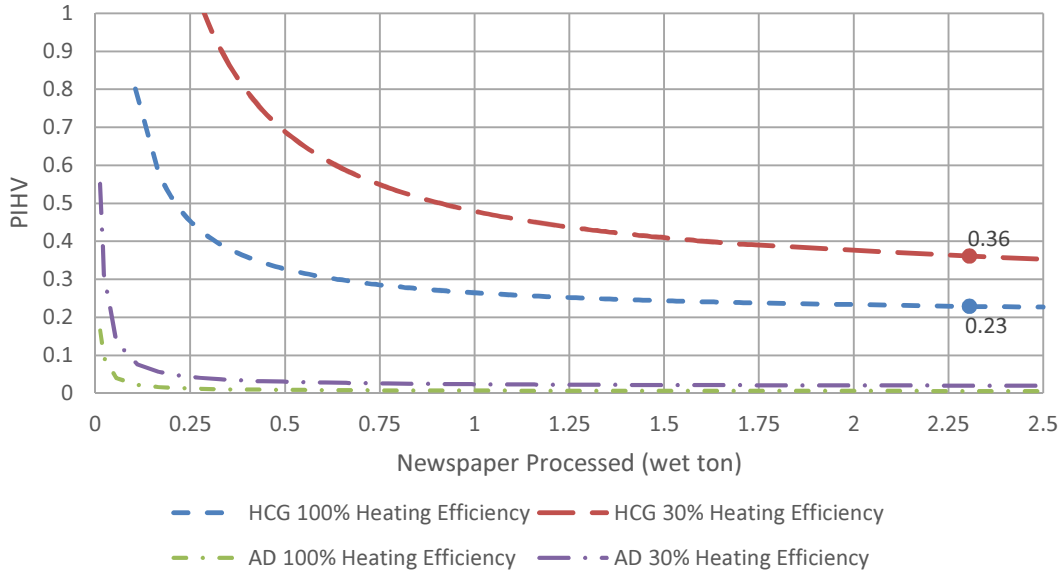

Figure B.5 Comparison of Energy Use for HCG and AD, in terms of Percentage of Inherent Heating Value (PIHV), with Heating Efficiencies
(Assume 0% heat recovery, newspaper HHV of 19.674 kJ/g (Worrell and Vesilind, 2011))

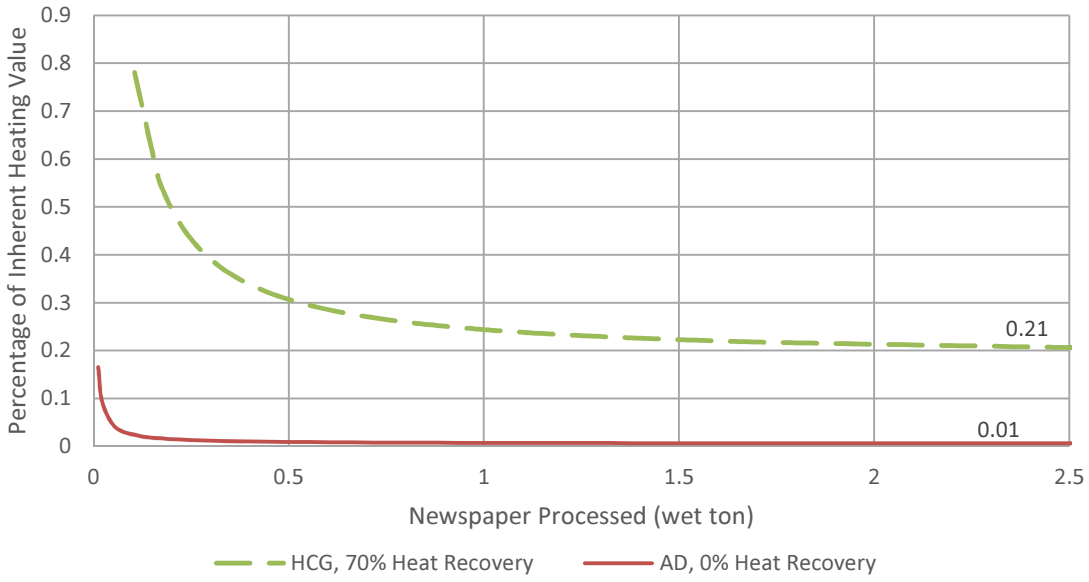

Figure B.6 Comparison of Energy Use for HCG and AD, in terms of Percentage of Inherent Heating Value (PIHV), with Heat Recovery
(Assume 0% heat recovery, newspaper HHV of 19.674 kJ/g (Worrell and Vesilind, 2011))

In contrast to AD, the embedded and operational energy costs for HCG represent a significant fraction of the energetic content of the feedstock. Nevertheless, HCG can extract at least 2x more energy than AD.